PRINCIPLES OF DYEING

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PRINCIPLES OF DYEING

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PREFACE

THIS book is the result of two years' instruction in dyeing, in the class room and in the laboratory. It aims to be a systematic presentation of the principles underlying the art of dyeing, illustrated and emphasized by laboratory exercises. It attempts to apply to the teaching of dyeing the same methods of class-room work, coördinated with experiments in the laboratory, which have proved so successful in the teaching of inorganic chemistry and other branches of science.

The reader will not find in this book, therefore, a collection of recipes for the production of particular colors, or detailed descriptions of more than a few of the more important processes of dyeing, or even a list of the multitude of dyes which are at the service of the dyer. For information on these points, special works, or manuals of dyeing, must be consulted. A clear survey of the field of dyeing does not require these things; rather, a multitude of details would obscure the general view which it is desired to present.

While intended primarily for the student, it is believed that this work will prove of benefit to the practical dyer who desires a fuller knowledge of the principles underlying his art. The experiments hardly call for more apparatus and reagents than a dyer should possess for the purpose of making necessary tests of his dyes and chemicals.

The experiments, so far as is practicable, are the processes used in dye-house work; necessarily modified for use as laboratory experiments. It has seemed desirable to reduce the time of the operations, so as to admit of the performance of a larger number of experiments by the student in the time at his disposal. Samples of all dyed material should be pasted in a suitable scrap-book, and marked with the name of the dye and the process used for dyeing. The dyed samples used for fastness tests, and all other samples possible, should be entered in the scrap-book and suitably marked, so that the pages of the scrap-book will exhibit a complete record of the student's work. In addition, a note-book should be kept, with descriptions of the experiments, observations, results, and answers to questions, after the manner of note-books used for experimental inorganic chemistry.

Before entering on this course, all students should be tested for *color-blindness*.

In the preparation of this book, a number of books and original articles have been consulted. It is impossible to make special acknowledgment to all of these, but the following deserve particular mention: Knecht, Rawson, and Lowenthal's "Manual of Dyeing," Hummel's "Dyeing of Textile Fabrics," Paterson's "Science of Color Mixing," Gardner's "Mercerization der Baumwolle," Beech's "Dyeing of Cotton Fabrics," and the publications of the Cassela Color Company, the Farbewerke Hoechst (Victor Koechl, United States agent), the Berlin Aniline Works, and the Farbenfabriken von Elberfeld. Acknowledgment is due also to Messrs. P. R. French and E. B. Owen for reading manuscript and proofs, and Professor W. A. Withers and Professor D. H. Hill for suggestions.

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CONTENTS

CHAPTER I

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

CHAPTER VI

CHAPTER VII

CHAPTER VIII

CHAPTER IX

CHAPTER XIV

CHAPTER XV

CHAPTER XVI

CHAPTER XVII

CHAPTER XVIII

CHAPTER XIX

CHAPTER XX

CHAPTER XXI

CHAPTER XXII

LIST OF ILLUSTRATIONS

PRINCIPLES OF DYEING

CHAPTER I

INTRODUCTION

THE term "dyeing," in its broad sense, covers the coloring of leather, paper, feathers, and other articles, besides the coloring of textile fabrics.

This book will be confined to a discussion of the dyeing of textile fibers, both the raw material and the finished fabric.

Object of the Dyer. — The object of the dyer is to produce any desired color on the material given him, an object usually accomplished by means of dyes, but sometimes by the use of bleaching agents, such as in the case of the production of a white piece of goods. The dyer is usually furnished with a sample of goods of the exact shade desired; but besides matching the sample, the color he produces must come up to certain requirements as regards fastness, cost, etc. In some cases it does not matter if the color washes out with water, provided it resists the action of light; while in other cases the color must be as fast to soap and hot water as possible. These requirements are met by the selection of different dyes and methods of dyeing, according to the demands of the work.

The color produced by the dyer must also be such that it will not undergo undesirable changes during the further manufacture of the goods, or in any of the finishing processes to which they may be subjected. For example, the color must not rub off from dyed threads to uncolored threads, giving the goods a dirty appearance, or change while the goods are being dried or ironed.

Laws of Dyeing. — The laws of dyeing rest, on the one hand, on the chemistry and physics of the dyes and textile fibers, and, on the other hand, on the principles involved in the application of the dye to the fiber. The different textile fibers have their individual peculiarities, and differ in their behavior toward the same dye; processes which are beneficial to one fiber may be positively injurious to another. Dyes also differ greatly in their behavior to fibers, and require different methods of application according to their nature.

Textile Fibers. — Cotton, wool, silk, linen, etc., are known as textile fibers. The only common property of all the textile fibers is their fibrous nature. They are divided into three groups: —

I. Mineral fibers; examples, asbestos, glass wool, and slag-wool.
II. Animal fibers; examples, silk and wool.
III. Vegetable fibers; examples, cotton, linen, and jute.

Mineral Fibers are incombustible; they are never dyed or bleached, and are only mentioned for the sake of completeness. *Asbestos* is a natural silicate of calcium and magnesium, and, on account of its being a non-conductor of heat, is used principally as a covering for steam-pipes. *Glass wool* is spun glass. *Slag-wool*, obtained by blowing a strong current of air through a stream of molten slag, is used for covering steam-pipes.

Animal Fibers. — Silk and wool are the two principal members of the group; wool is the outer covering of the sheep, and silk is the product of a caterpillar. The animal fibers contain carbon, hydrogen, nitrogen, and oxygen; wool contains sulphur in addition. In their action toward dyes and in other of their properties, animal fibers are quite different from vegetable fibers, as will be brought out later.

Leather, feathers, bone, horn, and ivory resemble the animal fibers in many of their properties, and behave in a similar way to dyes.

Vegetable Fibers. — Most of the vegetable fibers are obtained from the stem or leaves of plants, but the most important one — cotton — consists of the hairs which surround the seeds of a species of plant (Gossypium). The vegetable fiber next in importance to cotton is linen, then come hemp, jute, and China grass. The vegetable fibers contain carbon, hydrogen, and oxygen, but no nitrogen or sulphur. They do not have as much chemical activity as the animal fibers.

Straw (for hats), vegetable ivory (for buttons), wood, and paper resemble the vegetable fibers in their properties, and may be placed in the same class.

Artificial Fibers. — Imitation silks, spun artificially, have attained some commercial importance. They will be discussed later.

Coloring Matters. — According to their origin, coloring matters may be divided into two classes — natural and artificial.

The natural colors are of vegetable or of animal nature, though the only animal dye of any importance is cochineal, which is found in a bug.

Until about fifty years ago, the dyer was obliged to rely entirely upon natural colors, and some few mineral colors, to produce the effect desired. In 1856 the first artificial color (mauveine) was manufactured by W. H. Perkins, and captivated the world by its purity and beauty. Soon others were prepared, and a very large number of highly colored organic compounds are now known, though they do not all find practical application as dyes. The number of artificial dyes is increasing so rapidly every year that it is difficult to keep up with the new dyes which are constantly being put on the market.

Another advance made in recent years has been the discovery of methods for the preparation of natural coloring matters in the factory, the first one so prepared being alizarin. Alizarin is the coloring principle of the *madder* plant, which had been used for a long period to produce a fiery red color upon cotton goods. At present the artificial color has replaced the natural one almost completely. Indigo, a very important blue dye, is another natural dye which is being prepared by chemical methods, and just now there is a decided competition between the natural indigo and the artificial or synthetic indigo.

Plan of Study. — At present an enormous number of coloring matters are known, and the number is increasing rapidly. The matter is still further complicated by the fact that the same dye is often sold under several different names, and in different degrees of purity. The large number of dyes known need not, however, be a source of uneasiness to the student. The dyer does not need to be acquainted with every individual color, but should have a knowledge of the most important colors, and know how to test new dyes and work out new processes.

Without regard to their origin or chemical constitution, coloring matters can be separated into a number of groups for convenience in study, just as we can separate the elements into groups; as, for example, the chlorine group, including chlorine, bromine, and iodine; the oxygen group, in which are included sulphur, selenium, and tellerium. The members of these groups have certain resemblances to each other, and also their peculiarities, which distinguish them from the other members.

It is the object of this work to present a clear view of the subject of bleaching and dyeing of textile fibers. It is proposed to consider only a comparatively small number of dyes, either important in themselves, or those which can be used to emphasize important principles. In general, detailed information regarding particular dyes will not be given. It would hardly be profitable for the beginner to burden his mind with too many details at first, — he may thereby lose the general view, which it is important that he should gain quickly. Nevertheless, seemingly unimportant details, neglect of which may make or mar the work of the dyer, have been emphasized. It is the attention to details, which must be learned, and learned well, which makes the good dyer.

The plan of study which will be followed is briefly this: —

Of the first group of dyes, two will be studied with special attention to their action toward the different fibers. Members of the second group of dyes will then be taken up, and so on, until all the groups have been considered.

A clear idea of the relations between the groups of dyes, their general properties, and their behavior toward different fibers having been gained in this way, the next step will be the study of the groups of textile fibers.

Following this will come the consideration of the machinery for dyeing and bleaching, and the methods of preparing the fibers or fabrics for the dyeing proper. Finally the different groups of dyes will be studied, with the principles involved in their application to the different classes of material.

CHAPTER II

CONGO RED — PRIMULINE

Congo red, or congo, was discovered in 1884, and was the first artificial dye known to have the property of dyeing cotton directly without the aid of any other substance. For this reason other dyes of the same kind, which were afterward discovered, are sometimes called congo colors.

Properties. — Congo red is a red-brown powder, readily soluble in water. Its solubility is decreased by the presence of salts, — such as common salt (sodium chloride) or Glauber's salt (sodium sulphate). Salt in sufficient quantity will precipitate the dye from solution.

Experiment 1. — Dissolve a little congo red in 200 cc. water. Add common salt to a portion of the solution, stirring from time to time, until no more dissolves. Let the solution stand for half an hour, stirring occasionally, and filter. The first few drops may be colored, but the remainder of the filtrate will be nearly colorless. The dye has been "salted out" from solution.

Practical application is made of the power of salts to precipitate dyes and other compounds from solution in the manufacture of dyestuffs and other substances. In dyeing with congo and similar colors, salts are usually added to the dye-bath to decrease the solubility of the dye, and cause more of it to go upon the fiber.

Action of Acids. — Congo is the sodium salt of a dibasic acid. If we add hydrochloric acid to a solution of congo, the free color acid (combined with hydrochloric acid) separates as a dark-blue, flocculent precipitate. The reaction is as follows: —

$$\underset{\text{Congo red.}}{C_{32}H_{22}N_6S_2O_6Na_2} + 2\,HCl = \underset{\text{Color acid.}}{C_{32}H_{22}N_6S_2O_6H_2} + 2\,Na\,Cl.$$

Or, if we let $Ac\,Na_2$ represent congo red, the reaction may be written in a condensed form: —

$$AcNa_2 + 2\,HCl = AcH_2 + 2\,Na\,Cl.$$

Ac merely stands for a complex group of atoms of acid nature.

If the blue precipitate is treated with sodium hydroxide, it dissolves, congo red being formed again.

Experiment 2. — Add hydrochloric acid to a solution of congo red. Explain what happens, and write condensed reaction.

The acids always present in the air, especially in the air of cities, cause the bright color of goods dyed with congo to become dull gradually by liberating the free color acid; an effect which can be counteracted, to a certain extent, by saturating the goods, before drying, with a solution of sodium carbonate, which neutralizes the acid.

Reduction of Congo. — Reducing agents, such as zinc dust and acetic acid, transform congo red into colorless bodies.

Experiment 3. — To about 20 cc. of a solution of congo red add 20 cc. acetic acid (25 per cent) (what happens?), and then about 5 g. zinc dust. Mix well, heat to boiling, and boil a few minutes. Filter. Explain results.

The reaction between acetic acid and zinc dust is as follows: —

$$\underset{\text{Acetic acid.}}{2\,HC_2H_3O_2} + Zn = \underset{\text{Zinc acetate.}}{Zn(C_2H_3O_2)_2} + 2\,H.$$

The nascent hydrogen is taken up by congo red, and splits it into two new colorless compounds. All organic coloring matters may be reduced to colorless compounds by suitable choice of reducing agents. They vary greatly in the ease with which the reduction may be effected.

Behavior to Fibers. — If we boil cotton or wool with a solution of congo red, the fiber will withdraw a portion of the dye from solution, and become colored. Further, the color cannot be washed out with water. The dye has an affinity for the substance of the fiber, and dyes it; such dyes are called *direct* colors or *substantive* colors.

Experiment 4. — Boil five 10-gram skeins of cotton yarn with 500 cc. water and 1 g. sodium carbonate until they are thoroughly wet. Wash them and place them in clean water until needed. Cotton yarn should always be "boiled off" or "wetted out" before dyeing.

Prepare a dye-bath with 2 per cent (of the weight of the yarn) congo red,[1] 2 per cent sodium carbonate, and 20 per cent Glauber's salt (sodium sulphate), and make the volume up to 200 cc. Hang a 10-gram skein of cotton yarn in the bath on a V-shaped glass rod, and boil gently half an hour, working the yarn from time to time by lifting it out of the cup, and turning it with the aid of a glass rod. Remove, rinse, and dry. Save the dye-bath.

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[1] To save time, dyes and salts are furnished in solution, so that the student has only to measure out a certain volume of liquid. For example, 25 cc. congo solution contains 0.1 g.; 10 cc. sodium carbonate solution contains 0.1 g.; sodium sulphate (anhydrous) 5 cc. = 0.1 g. The dyeings are usually made in agate-ware cups, ½-pint capacity, heated directly by the burner.

Dye a 5-gram skein of wool in the same way, without the sodium carbonate. Which skein is the darker? Compare the dye-baths. Which fiber takes up the more dye?

If we examine the two solutions after dyeing cotton and wool with congo, we find:—

1. The wool has *exhausted* the dye-bath; that is, it has withdrawn almost all dyestuff from solution.

2. The cotton has not exhausted the bath, but has left a considerable portion of the dye unabsorbed.

The experiment illustrates the characteristic differences between animal and vegetable fibers in their behavior toward direct dyes. Animal fibers, represented by wool, have a great affinity for direct colors, and withdraw them readily and completely from solution. Vegetable fibers have no great affinity for them, and rarely exhaust a dye-bath.

It is evident that if we throw away the dye-bath after dyeing cotton with congo red or similar colors, a part of the dye is lost. In dyeing with such colors, the dye-bath is used continuously whenever possible, its strength being restored by fresh additions of dyestuff and salts after each dyeing.

Function of the Salts.—In dyeing with congo red and similar colors, salts are always added to the dye-bath.

Glauber's salt or common salt is added to decrease the solubility of the dye, and thereby cause more of it to go on the fiber. Sodium carbonate is added to make the bath alkaline and to counteract to some extent the action of acids of the air, as the sodium carbonate is not entirely washed out.

Action of Hard Water. — The calcium and magnesium salts of the color acid of congo red are not soluble in water, and are precipitated when a calcium or magnesium salt and congo red are brought together in solution.

Water containing calcium salts (hard water), when used for the preparation of a dye-bath, precipitates congo red with loss to the dyer.

Experiment 5. — Dissolve 0.1 g. congo in 75 cc. water, add 25 cc. lime-water, and boil about 10 minutes. What is the precipitate?

Prepare two dye-baths, each with exactly 2 per cent congo (measure the solution with a pipette), 2 per cent sodium carbonate, and 20 per cent sodium sulphate. Add 50 cc. lime-water to one solution and make the volume of each 200 cc. Dye two skeins of cotton yarn (boiled out) as described in Experiment 4. What is the effect of hard water?

Hard Water. — The purest water found in nature is rain-water. As soon as rain-water comes in contact with the earth, and begins its course toward the ocean, it begins to take up various substances, according to the character of the soil with which it comes in contact. Natural waters which come in contact with limestone (calcium carbonate) gradually take up more or less of the carbonate with the aid of the carbonic acid of the air, forming calcium acid carbonate, $Ca(H\,CO_3)_2$, and becoming hard. On heating the water, this salt decomposes, carbon dioxide is given off, and calcium carbonate is precipitated. The hardness removed by boiling is called the *temporary hardness*.

Water, when it comes in contact with calcium sulphate, dissolves it, and a hard water is produced, the hardness of which is not removed by boiling, and is therefore called *permanent hardness.* Magnesium sulphate acts in the same way to produce permanent hardness.

By boiling hard water with sodium carbonate or soap, insoluble calcium compounds are precipitated and soft water can be drawn off. These, and other methods of purifying water, will be discussed later.

Hard water is often injurious in dyeing.

Stripping of Congo. — When cotton yarn dyed with congo is boiled in water, part of the color will be removed or *stripped* from the fiber.

Experiment 6. — Plait part of the cotton yarn dyed with congo with undyed cotton yarn, place it in 50 cc. water, and boil 15 minutes. Proceed with dyed wool in the same way, plaiting it with wool yarn. Which fiber loses its color more easily?

The experiment shows that the color is more easily stripped from cotton than from wool. It also shows, in the case of the cotton yarn, that part of the color stripped off is taken up by undyed fibers; the dyed and undyed yarn will become the same color if boiled long enough with water.

Behavior to Washing, Light, etc. — If we subject the dyed yarn to the action of warm water and soap, — that is, imitate the action of washing, — the solution becomes colored, but the color of the yarn does not fade appreciably. If white material is present, it becomes colored; the color is said to *bleed.*

Experiment 7. — The test for fastness to washing is conducted as follows: —

Plait part of the dyed cotton with undyed yarn. Make up a solution[1] of 10 g. soap in a liter of water, heat to 60° C., and pour about 25 cc. on the yarn. The plait should be worked and squeezed in the liquid, and allowed to remain in it 10 minutes. It is then rinsed in cold water, allowed to lie in water 15 minutes, then wrung out, washed, and dried. Note any change in the color of the yarn, how much color is taken up by the soap, and whether the color bleeds. Test the dyeing on wool in the same way.

Congo is much faster to washing on wool than on cotton.

If a skein of yarn dyed with congo is placed in the sunshine, after a time the color will fade. In time the color would be almost completely destroyed. All dyes are affected by light, but vary in their resistance toward it; the nature of the material dyed (cotton or wool, etc.) is also of effect.

EXPERIMENT 8. — Expose some of the dyed yarn to direct sunshine for several days.

Dyes are also tested for their fastness to acids. The test represents their resistance to acids of the air, and perspiration.

EXPERIMENT 9. — Steep portions of the dyed yarns in about 10 cc. of a 25 per cent solution of acetic acid for about 5 minutes. Wring out, wash, and dry. Explain any change in color.

Another test is for fastness to alkalies: —

EXPERIMENT 10. — Steep portions of the dyed yarn for 5 minutes in 25 cc. of a 1 per cent solution of sodium carbonate, wash and dry.

Fastness. — By the fastness of a color to washing, we mean its permanence when subjected to friction, and the action of a warm solution of soap (Experiment 7). In the

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[1] A warm solution of soap for this test should be kept on hand in the laboratory.

same way we speak of fastness to light, to acids, to alkalies, and to other influences. According to the behavior of the color, it is characterized as fugitive (easily affected), moderately fast, fairly fast, and very fast.

The term "fast," as applied to a piece of goods, means that the color will not fade under ordinary usage. What will be required of the color depends upon the use to which the material is to be put. The color of a shirt must be fast to washing and light; coat linings may not be washed, but the color must not rub off. Underwear must be fast to perspiration and washing. Carpets and curtains must withstand the action of light. It is perfectly plain that a dye may be very fast when applied to one class of material, and fugitive when applied to another class.

Direct Cotton Colors. — Congo is a member of a class of dyes known as direct cotton colors, or substantive cotton colors, which will dye cotton, wool, or any other fibre without the aid of other substances. There are dyes which are direct colors for wool and silk, but not for cotton; hence these dyes are called direct *cotton* colors.

The direct cotton colors, as a rule, resemble congo in their behavior toward acids, alkalies, salts, hard water, and the textile fibers. They are dyed in much the same way, as a rule "bleed" into white material, and are faster in wool than in cotton. Cotton never removes these colors completely from the dye-bath.

Primuline. — Primuline is a direct cotton color which was discovered in 1888. It is sometimes called carnotin, polychromin, and aureotin. Thiochromogen is claimed to be a very pure form of primuline.

Properties. — Primuline is a yellow powder, readily soluble in hot water, less soluble in cold. Like congo, it can be "salted out" of solution by sodium sulphate, sodium chloride, or other salts.

Like congo, primuline is the sodium salt of a color acid. The free acid is precipitated as a dark yellow flocculent mass when hydrochloric acid or sulphuric acid is added to a solution of the dye.

Experiment 11. — Dissolve a little primuline in water. Salt out a portion of the solution as in Experiment 1. To another portion of the solution add hydrochloric acid, and heat gently. The precipitate is the free color acid.

When primuline is dissolved in concentrated sulphuric acid, it forms a liquid, which appears yellow if the light which reaches the eye passes through the solution, blue if it is reflected from the surface of the liquid. It has a blue fluorescence. If the solution is poured into water, an orange-yellow precipitate is formed.

The behavior of dyes toward concentrated sulphuric acid is a useful aid in their identification. The test is carried out as follows: —

Experiment 12. — Dissolve a small quantity of primuline in concentrated sulphuric acid, and note the color of the solution. Pour a portion of it into water. Heat another portion nearly to boiling, observing any changes, and (*caution!*) pour it into cold water.

Behavior toward Fibers. — Primuline is dyed on cotton, like congo red, in a bath with the addition of salts. It dyes a greenish yellow color, which is somewhat faster to washing than congo. The bath is not exhausted.

The direct dyeings of primuline are of little interest. It is usually converted into other dyes by a process called *diazotizing and developing*.

Diazotizing and Developing. — When goods dyed with primuline are treated first with a solution of nitrous acid, and then with a developer, new dyes are produced with new properties. They are insoluble in water, and valuable on account of being fast to washing. The process is called diazotizing and developing.

Direct cotton colors and other bodies which can be diazotized and developed contain the group NH_2. They are related to ammonia, and may be regarded as ammonia in which one atom of hydrogen has been replaced by a complex group of atoms, as $C_6H_5NH_2$, aniline. When these substances are treated with nitrous acid, the two combine to form a diazonium salt: —

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5NH_2HCl} + HNO_2 = \underset{\text{Phenyl diazonium chloride.}}{C_6H_5N_2Cl} + 2\ H_2O\,;$$

or, for any of these compounds: —

$$RNH_2HCl + HNO_2 = RN_2Cl + 2\ H_2O.$$

Diazonium compounds are, for the most part, very unstable, and even explosive in the solid state. Many of them decompose when the temperature is raised, and they easily enter into reactions.

When a diazonium salt is treated with a phenol, or an aromatic amine, under proper conditions, the two combine directly and a stable compound is formed. For example: —

$$\underset{\text{Diazonium chloride.}}{C_6H_5.N_2.Cl} + \underset{\text{Phenol.}}{C_6H_5OH} = \underset{\text{Azoxy benzene.}}{C_6H_5.N_2C_6H_4OH} + HCl.$$

This is the kind of action which takes place when a diazotized fabric is treated with a developer. The developer combines with the diazonium compound to form a more stable body, which is a new dye.

Experiment 13. — Dye five 10-gram skeins of boiled-out cotton yarn with primuline, as follows: Dissolve 4 per cent (of the weight of the yarn) primuline, 30 per cent salt, and 5 per cent sodium carbonate in 600 cc. water; heat, enter the yarn, and boil 30 minutes. Work from time to time. Is the bath exhausted?

Diazotize four of the dyed skeins. Prepare a bath of 3 per cent sodium nitrite and 200 per cent dilute hydrochloric acid in 600 cc. water. Free nitrous acid is liberated according to the reaction: $NaNO_2 + HCl = NaCl + HNO_2$. Enter the yarn, and work 10 minutes. The diazotized primuline is very unstable, and must be developed as soon as possible. Rinse, and develop as described below.

Hang one skein of the yarn, after diazotizing and before developing, in the sunshine for 10 minutes, and then develop as in (*a*) below.

Developing. Have ready the following baths, enter one skein in each, work cold 10 minutes, wash, and dry.

(*a*) 1 per cent beta-naphthol[1] and 1 per cent sodium hydroxide in 200 cc. water.

(*b*) 1 per cent resorcin and 2 per cent sodium hydroxide in 200 cc. water.

(*c*) 2 per cent toluene diamine and 4 per cent sodium carbonate in 200 cc. water.

Tabulate your results.

The preceding experiment shows that different developers, acting upon diazotized primuline, produce different dyes of different colors. It also shows that light decomposes diazotized primuline, and prevents it from uniting with the developer.

Precautions in Diazotizing. — In diazotizing primuline, or any other body, the solution of nitrous acid must be

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[1] The solution provided contains beta-naphthol dissolved in an equal quantity of sodium hydroxide.

cold for two reasons. First, a warm solution would have an injurious effect upon the process of diazotizing, either by preventing it from taking place, or by decomposing the diazonium compound formed. Many diazonium compounds are stable only at a low temperature, and decompose immediately if the temperature is only slightly elevated. In the second place, nitrous acid is not readily soluble even in cold water, and would escape rapidly if the temperature is elevated.

For these two reasons, but more particularly the first, it is often necessary to cool the diazotizing bath by means of ice. Dyes which are diazotized and developed are sometimes called *ice colors*.

Another necessary precaution in diazotizing is that the bath should contain sufficient nitrous acid. Otherwise the primuline is diazotized only in part, and inferior colors result.

Developers. — The developers used for primuline are organic compounds, either amines, or phenols.

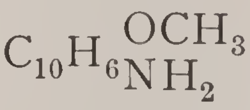
Amines are basic in nature, and unite with acids to form salts. Thus aniline, an amine, combines with hydrochloric acid to form aniline hydrochloride, a reaction resembling that between ammonia and the same acid.

$$C_6H_5NH_2 + HCl = C_6H_5NH_3Cl.$$
$$NH_3 + HCl = NH_4Cl.$$

Phenols are weakly acid in nature, forming salts with bases. Thus phenol forms sodium phenolate: —

$$C_6H_5OH + NaOH = C_6H_5ONa + H_2O.$$

The phenol most largely used in developing such colors as primuline is *beta-naphthol*. This is a compound having the formula $C_{10}H_7OH$, which is sold as a powder, or as lumps. It is only sparingly soluble in hot water, hardly soluble at all in cold water. It dissolves easily in caustic soda, a sodium salt, $C_{10}H_7ONa$, being formed. This compound is slowly oxidized by the air, and the solution becomes dark colored. Other developers are: —

Phenol	C_6H_5OH
Resorcin	$C_6H_4(OH)_2$
Alpha-naphthol	$C_{10}H_7OH$
Naphthalamine ether	 $C_{10}H_6\genfrac{}{}{0pt}{}{OCH_3}{NH_2}$
Phenylene diamine	$C_6H_4(NH_2)_2$
Toluene diamine	$C_7H_6(NH_2)_2$

Fastness of the Colors. — The colors produced by diazotizing and developing primuline are insoluble in water; hence they are fast to washing, and do not bleed. Very little of the color is removed even by boiling water. They are little affected by acids or alkalies, but are affected by light.

EXPERIMENT 14. — Test the fastness of the direct dyeings and the diazotized and developed dyeings of primuline to boiling water, washing, acids, and alkalies, as described in Experiments 6, 7, 9, and 10.

Summary. — Primuline is an important member of a group of direct cotton colors which are diazotized and developed to produce colors highly fast to washing. They resemble primuline in many particulars.

CHAPTER III

FUCHSINE

Fuchsine, or magenta, was discovered in 1859, being one of the first artificial dyes made. One method of preparing it is by oxidizing a mixture of aniline and toluidine, which can be made from compounds found in coal tar. The crude product is dissolved in hot water and allowed to cool, when the dye crystallizes out and is separated. The solution, or "mother liquor," as it is called, which contains some of the dye mixed with other substances, is evaporated and less pure grades of fuchsine are obtained, which are sold under various names, such as cerise, grenadine, amaranth, etc.

Composition. — Fuchsine, like almost all dyes in general use, comes into commerce in varying degrees of purity. When pure, it consists of a mixture of the hydrochloric acid salts of two bases, para-rosaniline, and rosaniline; rosaniline is present in greater quantities, and, for the sake of clearness, we shall speak of fuchsine as if it contained rosaniline only.

Properties. — Fuchsine appears as a powder, or as crystalline masses, with a brilliant green metallic luster. It is soluble in 250 parts water, much more readily in alcohol. It dissolves in concentrated sulphuric acid with a brownish yellow color; the solution becomes nearly colorless on dilution with water.

Sodium or potassium hydroxide added to a solution of fuchsine precipitates a mixture of the two bases, pararosaniline and rosaniline, as a reddish brown precipitate. With a weak solution of fuchsine, no precipitate appears; the solution becomes colorless.

$$C_{20}H_{20}N_3Cl + NaOH = \underset{\text{Rosaniline base.}}{C_{20}H_{20}N_3OH} + NaCl;$$

or, condensed:—

$$BCl + NaOH = BOH + NaCl.$$

When strong hydrochloric or sulphuric acid is added to a solution of fuchsine, it changes color, becoming orange-yellow to colorless, according to the strength of the solution. If the solution is heated, it again becomes pink. The first change is due to the formation of acid salts of rosaniline, which are orange-yellow, as for example:—

$$\underset{\text{Fuchsine.}}{C_{20}H_{20}N_3Cl} + 2\,HCl = \underset{\text{Acid salt.}}{C_{20}H_{20}N_3Cl \,.\, 2\,HCl};$$

or, abbreviated:—

$$BCl + 2\,HCl = BCl \,.\, 2\,HCl.$$

The acid salt is decomposed into fuchsine and acid when it is heated, or diluted with water. A great many dyes behave in the same way, forming acid salts which are different in color from the basic salts, and are easily decomposed. *Acetic acid* does not, as a rule, produce such salts.

Leuco Compounds.—If we heat a solution of fuchsine with zinc and acetic acid, the solution is decolorized. Congo red behaves in the same way. In the case of fuchsine the nascent hydrogen combines with the color, forming leuco-rosaniline hydrochloride, which is colorless.

$$\underset{\text{Fuchsine.}}{C_{20}H_{20}N_3Cl} + 2\ H = \underset{\text{Leuco-rosaniline hydrochloride.}}{C_{20}H_{21}N_3HCl};$$

or, condensed: —

$$BCl + 2\ H = H_2BCl.$$

When this colorless compound is brought in contact with oxidizing agents, such as chromic acid, it loses hydrogen and is again converted into fuchsine.

$$C_{20}H_{21}N_3HCl + O = C_{20}H_{20}N_3Cl + H_2O;$$

or, abbreviated: —

$$H_2BCl + O = BCl + H_2O.$$

Leuco-rosaniline is also oxidized very slowly by the air.

A colorless body which is formed from a colored compound by the addition of hydrogen to its molecule, and which loses its hydrogen by oxidation, forming the original colored body, is called a *leuco* compound, the word "leuco" meaning white or colorless.

Many dyes are reduced, like fuchsine, to leuco bodies; on the other hand, others, like congo, are broken up by reducing agents, and the product cannot be oxidized back to the original coloring matter. This property is an aid in the identification of dyestuffs.

EXPERIMENT 15. — Examine some fuchsine and describe its appearance. Dissolve a little in concentrated sulphuric acid and note the color. Pour the solution into water (color).

Dissolve a little of the dyestuff in hot water. Add hydrochloric acid to a portion of the solution, and allow it to stand fifteen minutes. Explain what happens. Heat the acid solution. Explain.

To another part of the solution, add sodium hydroxide and heat gently. Explain. Write condensed reactions.

Add zinc dust and acetic acid (see Exp. 3) to a portion of the solution, and heat it to boiling 10 minutes. Explain. Filter the solution and saturate a filter paper with it. Touch the paper with a glass rod moistened with a solution of chromic acid, and observe it after several hours. What happens?

Rosaniline Tannate. — Rosaniline and tannic acid unite to produce a salt, or *lake* as it is called, which is not soluble in water, but is soluble in acids, such as hydrochloric acid, acetic acid, or an excess of tannic acid. The lake is formed when solutions of tannic acid and fuchsine are brought together: —

$$\underset{\text{Fuchsine.}}{2\,C_{20}H_{20}N_3Cl} + \underset{\text{Tannic acid.}}{H_2C_{14}H_8O_9} = \underset{\text{Rosaniline tannate.}}{(C_{20}H_{20}N_3)_2C_{14}H_8O_9} + 2\,HCl.$$

In the condensed form, the reaction is written: —

$$2\,BCl + H_2Ac = B_2Ac + 2\,HCl.$$

EXPERIMENT 16. — Add a few drops of a solution of tannic acid to a solution of fuchsine, and heat gently. What happens? Divide the solution into two portions; to one add an excess of tannic acid, and to the other add hydrochloric acid. What happens?

Other Salts. — Fuchsine sometimes occurs in commerce as rosaniline acetate, sulphate, or nitrate. Other salts may be prepared.

Fuchsine combines with some direct cotton colors, like congo, to form insoluble salts, or lakes: —

$$BCl + AcNa = BAc + NaCl.$$

Action toward Fibers. — Fuchsine is a direct dye for wool, but not for cotton. Wool takes it up readily, and exhausts the bath. Cotton is indeed stained when boiled with fuchsine, but the color is rapidly removed by washing.

Experiment 17. — Dye a 5-gram skein of wool in 1 per cent fuchsine in 200 cc. water. Heat to boiling 30 minutes, remove, wash, and dry. Is the bath exhausted?

Dye a 10-gram skein of cotton in the same way, but dry without washing. Then wash a portion of the skein with water.

Test the fastness of fuchsine on wool to washing (Exp. 7), acids (Exp. 9), and alkalies (Exp. 10).

Dyeing Cotton with Fuchsine. — Fuchsine is sometimes applied to cotton for the production of light tints by working the fiber in a hot solution of the dye, and drying it without washing. The bath is not exhausted, and the color is easily removed by washing. This method may be called *dyeing by saturation*, as the material is simply dried while saturated with a solution of the dye for which it has no affinity.

Another method, seldom used, is to *animalize* the fiber, *i.e.* give it the properties of an animal fiber. The cotton is saturated with a solution of albumen (from eggs or blood), and passed through hot water, which coagulates the albumen and renders it insoluble. The coating of albumen on the surface of the fiber has an affinity for fuchsine, and similar dyes, and withdraws it from solution, exhausting the bath.

The chief methods for dyeing cotton with fuchsine are to produce an insoluble tannate of the color on the fiber, or to form insoluble salts with the color acids of direct cotton colors.

Mordants. — Cotton absorbs tannic acid from solution, and when afterwards brought in contact with fuchsine, withdraws the dye from solution, and is dyed. The dyeing is due to the affinity of the tannic acid for the dyestuff, not to direct absorption by the fiber. Rosaniline tannate is produced in an insoluble form within the fiber. A substance which, like tannic acid, unites with a dye to fix it upon a fiber, is called a *mordant*. The compound of dye and mordant is a *lake*.

Turkey-red oil is another mordant used sometimes to fix basic dyes upon cotton. It is a mixture of fatty acids prepared by treating castor oil with sulphuric acid.

Direct cotton colors may serve as mordants for fuchsine and similar colors.

Fixing Tannic Acid. — When tannic acid acts upon fuchsine, there is always a liberation of hydrochloric acid, which prevents the reaction from being complete, as the lake is soluble in acid: —

$$2\,BCl + H_2Ac = B_2Ac + 2\,HCl.$$

Insoluble metallic tannates possess an attraction for fuchsine equal to tannic acid, if not greater. The presence of the metal aids in the decomposition by reason of a portion neutralizing the liberated acid of the coloring matter, and it is probable that a very insoluble tannate of the metal and color base is produced. The process of converting tannic acid into insoluble metallic salts is termed *fixing*, and is usually carried out after mordanting with tannic acid. Salts of antimony, iron, and sometimes tin are used as fixing agents.

Antimony tannate is colorless, and gives the brightest and fastest colors. It is produced by treating the goods mordanted with tannic acid with a solution of antimonyl potassium tartrate (tartar emetic) or other antimony salts. The reaction is as follows: —

$$\underset{\text{Tartar emetic.}}{2\ KSbOC_4H_4O_6} + \underset{\text{Tannic acid.}}{H_2C_{14}H_8O_9} = \underset{\text{Potassium acid tartrate.}}{2\ KHC_4H_4O_6} + \underset{\text{Antimony tannate.}}{(SbO)_2C_{14}H_8O_9}.$$

The bath becomes acid from the formation of potassium acid tartrate, which, after a time, prevents the reaction from going further. It can be neutralized with soda.

Iron tannate is dark in color, being the basis of most black inks. It is produced by the action of ferrous sulphate or other iron salts upon tannic acid: —

$$FeSO_4 + H_2C_{14}H_8O_9 = FeC_{14}H_8O_9 + H_2SO_4.$$

The ferrous tannate is oxidized by the air.

The reaction does not go far unless the sulphuric acid is from time to time neutralized with sodium carbonate. Or the acid is neutralized as fast as it forms if chalk is added to the bath. Iron tannate can be used only in fixing tannic acid for very dark colors.

EXPERIMENT 18. — Boil three 10-gram skeins of cotton yarn with 5 per cent tannic acid dissolved in 500 cc. water, until the cotton is thoroughly wetted out, at least 15 minutes. Allow the solution to cool an hour, working the yarn from time to time. Tannic acid is absorbed more readily by cotton from a cold solution. Squeeze well, and proceed as below: —

Skein No. 1. Dye as directed below.

Skein No. 2. Fix with antimony, by working 10 minutes in a bath of 2 per cent tartar emetic in 200 cc. water. What is formed? Wash well, and dye as directed below.

Skein No. 3. Fix with iron, by working 10 minutes in a bath of 5 per cent copperas and 3 per cent calcium carbonate in 200 cc. water. What is formed? Wash well and dye.

Prepare three dye-baths, each with 1 per cent fuchsine in 200 cc. water. Enter a skein in each bath, raise the temperature to 65° C., and keep at this temperature 20 minutes. The yarn should be worked carefully. Squeeze, and dry without washing.

How do the three skeins differ in color? Test fastness to washing, acids, and alkalies as directed in Experiments 7, 8, and 9. How do they differ in fastness?

Action of Hard Water. — The action of hard water in dyeing with fuchsine is illustrated by the following experiment: —

Experiment 19. — Prepare a dye-bath with 1 per cent fuchsine and 50 cc. lime-water in 200 cc. water, and dye a 5-gram skein of wool as directed in Experiment 17. Dye another skein in the same way, leaving out the lime-water. What is the difference?

Lime-water or hard water with temporary hardness precipitates fuchsine from solution as the free color base, and prevents a portion of it from going on the wool. The precipitate is liable to settle on the material and cause dark spots (*dye-spots*), which are difficult to remove.

The action of hard water on congo is due to the precipitation of the dyestuff in the form of an insoluble calcium salt; with fuchsine, the alkalinity of the water precipitates the insoluble color base. The causes and the remedies are different. In the case of congo, the hard water can be purified only by removal of calcium salts; in the case of fuchsine, the alkalinity of the water may be neutralized with an acid.

Printing Fuchsine. — Advantage is taken of the solubility of rosaniline tannates (and the tannates of similar colors), in acetic acid, in printing cotton cloth. The cloth is printed with a mixture of the dyestuff, tannic acid, acetic acid, and suitable thickening agents, and steamed. Acetic acid is driven off, and the tannate is fixed in an insoluble form. The cloth is then passed through a solution of tartar emetic, which completes the fixation.

Basic Colors. — Fuchsine is a representative of an important class of dyestuffs known as *basic colors*. They are all salts of color bases, direct dyes for wool but not for cotton, and are dyed on cotton with a tannic acid mordant, or other mordants of acid nature. Hard water has the effect of precipitating them as the free color base.

CHAPTER IV

BIEBRICH SCARLET — ALKALI BLUE

BIEBRICH scarlet is a scarlet dye. It is also called scarlet B, scarlet 3 RB or ponceau 3 RB, new red L, and imperial scarlet. The letters after the name of a dye sometimes indicate some particular brand or strength of color, sometimes indicate the hue of the dye. Thus, methyl violet B is a bluer shade than methyl violet R. The letters used are B for blue, R for red, G for yellow (German, *gelb*), or sometimes J (French, *jaune*), and V for violet.

Properties. — Biebrich scarlet occurs as a brown-red powder, easily soluble in water, forming an orange-red solution. It dissolves with a green color in concentrated sulphuric acid; diluted with water, the color changes from blue to red, and a red-brown precipitate separates.

Like congo and primuline, Biebrich scarlet is the sodium salt of a color acid. Hydrochloric acid precipitates the free color acid from solution in the form of a flocculent, dark red precipitate, unless the solution is very dilute: —

$$\underset{\text{Biebrich scarlet.}}{Na_2Ac} + 2\,HCl = \underset{\text{Color acid.}}{H_2Ac} + 2\,NaCl.$$

The aluminium and calcium salts are not soluble, and are precipitated when solutions of the dye and of calcium or aluminium salts are brought together.

Zinc dust and acetic acid reduce the dye to colorless bodies; a leuco compound is not formed.

Action toward Fibers. — Biebrich scarlet is a direct dye for silk and wool. It colors cotton to a certain extent, but the color washes out very readily with water. Silk and wool are dyed with Biebrich scarlet in an acid bath; in a neutral bath the dyeings are less bright, and the bath is not exhausted.

Experiment 20. — Dye a 5-gram skein of wool in a bath of 2 per cent Biebrich scarlet in 200 cc. water, boiling 15 minutes. Remove, rinse, and dry.

Dye another skein as directed above, with the addition of 2 per cent sulphuric acid. Compare the two skeins and the two dyebaths. What is the effect of the acid?

Action of the Acid. — The acid has a twofold action: in the first place, it liberates the color acid of the dye, which has a much greater affinity for wool than has its salts. In the second place, the acid acts chemically upon the wool, increasing its power to take up dye. Part of the acid is withdrawn from solution to enter into combination with the wool.

Experiment 21. — Boil a 5-gram skein of wool for 15 minutes in a bath of 10 per cent sulphuric acid in 200 cc. water. Wash thoroughly, and dye with 2 per cent Biebrich scarlet in 200 cc. water. Is the bath exhausted? Compare with the colors obtained in Experiment 20.

Dye a second skein with 2 per cent Biebrich scarlet and 0.3 per cent sulphuric acid in 200 cc. water. This quantity of acid is sufficient to liberate the free color acid. Is the bath exhausted?

Wool boiled with sulphuric acid can be dyed with Biebrich scarlet without any addition of acid to the bath, while if the acid added to the dye-bath is only in sufficient quantity to liberate the color acid, the wool is not dyed a full shade. In practice, about ten times as much acid is used as is needed to liberate the free color acid.

Assistants. — Sulphuric acid, sodium sulphate, sodium chloride, and other substances which aid in dyeing without actually entering into combination with the dyestuff to form a color lake, are termed *assistants*.

Stripping Biebrich Scarlet. — The dye is removed from wool by boiling it with a solution of ammonia, sodium carbonate, or ammonium acetate. Ammonium acetate or ammonia is preferred to sodium carbonate, which is liable to injure the fiber.

Experiment 22. — Boil half of a wool skein dyed with Biebrich scarlet with 2 per cent ammonium acetate in 100 cc. of water for half an hour. Is the color removed?

Dyeing Cotton. — Biebrich scarlet cannot be fixed upon cotton fast to washing. It is used to a considerable extent on account of its fastness to light in cases where fastness to water is not necessary. Cotton is dyed in several ways, of which the following may serve as examples: —

(*a*) Dyeing by saturation. The cotton is worked in a bath containing the dye and some salts, and dried without washing.

(*b*) Dyeing as aluminium salt. The cotton is boiled with a solution of the dye to which alum has been added. The dye is taken up in the form of an aluminium salt, which is less soluble in water than its sodium salt, and has greater affinity for the fiber. Darker colors are produced than by method (*a*).

(*c*) Dyeing on aluminium mordant. The cotton is worked in a solution of basic aluminium sulphate, formed by adding sodium carbonate to alum:—

$$4\,KAl(SO_4)_2 + 3\,Na_2CO_3 + 3\,H_2O = Al_4(SO_4)_3(OH)_6 + 3\,Na_2SO_4 + 3\,CO_2 + 2\,K_2SO_4.$$

The cotton decomposes this body, and absorbs it in the form of a still more basic salt. It is then worked in the dye-bath, when the dye is fixed in the form of its aluminium salt.

(*d*) Dyeing on tin mordant. The cotton is worked in sodium stannate, Na_2SnO_3, and then in basic aluminium sulphate. Stannic hydroxide and aluminium hydroxide are formed. The cotton is then dyed. In no case is the bath exhausted.

EXPERIMENT 23.—Dye skeins of boiled-off cotton yarn with Biebrich scarlet as follows and dry without washing:—

No. 1. Dye with 2 per cent Biebrich scarlet and 20 per cent salt in 200 cc. water, boiling 15 minutes.

No. 2. Dye with 2 per cent Biebrich scarlet, 20 per cent salt, and 25 per cent alum in 200 cc. water, boiling 15 minutes.

No. 3. Mordant by working carefully, in a bath of 10 per cent alum and 2 per cent sodium carbonate in 200 cc. water. (Reaction.) Wring out and dye, without washing, in a bath of 2 per cent Biebrich scarlet and 20 per cent salt in 200 cc. water. Enter the skein at 50° C., and work 15 minutes without further heating.

No. 4. Work 15 minutes in a bath of 5 per cent sodium stannate in 200 cc. water. Squeeze, and work 15 minutes in 5 per cent alum and 1 per cent sodium carbonate in 200 cc. water. Wring out, and dye as with skein No. 3.

How do these skeins differ in color? Test fastness to washing (Exp. 7). How do they compare?

Hard Water. — Biebrich scarlet is precipitated by hard water from neutral solutions, but not from acid solutions. Hence hard water interferes with the dyeing of cotton, but not with wool dyeing.

Alkali Blues. — The alkali blues, also called Nicholson's blue, and soluble aniline blue, are prepared by the action of sulphuric acid upon aniline blue, a basic color which is insoluble in water, but soluble in alcohol.

Composition. — The aniline blues, like fuchsine, are mixtures of several chemical compounds. There are several varieties, differing in color and composition. The brands are indicated by letters according to their shades. Thus we have alkali blue 6 B to 4 R, ranging from a greenish blue, the most valuable, to a red blue, or purple.

Properties. — The alkali blues appear as blue powders, 4 R being of a reddish cast. They are sparingly soluble in cold water, freely soluble in hot water. They dissolve in concentrated sulphuric acid to a red-brown solution; on diluting, a blue precipitate appears.

With sodium hydroxide, the solution becomes claret red.

With zinc and acetic acid, the corresponding leuco compound is formed.

Like congo and Biebrich scarlet, the alkali blues are salts of a color acid; the free color acid is precipitated when hydrochloric or sulphuric acid is added to a solution of the dye.

Alkali blue is precipitated by hard water.

Action toward Cotton and Wool. — The alkali blues are acid colors, and consequently cannot be dyed on cotton fast to washing. The methods for dyeing on cotton are the same as for Biebrich scarlet.

Alkali blue is removed from acid, alkaline, or neutral solutions by wool or other animal fibers, though, unless the bath is acid, it is not exhausted. On account of the fact that the color acid is nearly insoluble in water, wool and silk are always dyed with alkali blue in a bath made alkaline with borax. The color acid is liberated, and the proper color developed subsequently by a treatment with dilute sulphuric acid. The lower the temperature of the developing bath, the greener is the shade of blue obtained; if the temperature is raised, the shades become redder in tone.

Experiment 24. — Examine alkali blue. Dissolve some in water, and try the effect of sodium hydroxide and hydrochloric acid upon it.

Dye a 5-gram skein of woolen yarn in a bath of ½ per cent alkali blue 4 B and 2 per cent borax in 200 cc. water, boiling half an hour. Remove a sample for your scrap-book, and develop the remainder by working for a few minutes at 60° C. in a bath of 2 per cent sulphuric acid in 200 cc. water.

Dye another skein as directed above, with alkali blue 4 R, and develop with sulphuric acid at 80° C.

Test fastness of the developed colors to acids, alkalies, and washing (Exps. 7, 9, and 10). What is the effect of developing? What is the difference between the 6 B and the 4 R?

Acid Colors. — Biebrich scarlet and alkali blue are acid dyes. Congo and fuchsine are dyed in the form of salts, but Biebrich scarlet, alkali blue, and all other acid colors are dyed upon wool in the form of the color acid. They are dyed from an acid bath, or an alkaline bath, and in the latter case require an after treatment with acid to liberate the color acid and develop the color.

CHAPTER V

LOGWOOD

Logwood, or Campeachy wood, is the wood of a large tree which grows abundantly in the West Indies, Mexico, and parts of Central America. Logwood was introduced as a dye soon after the discovery of America.

Preparation. — Logwood is imported in logs weighing about 400 pounds. The fresh wood is colorless, or nearly so, and contains a glucoside, composed of hæmatoxylin and sugar. It is cut into chips or rasped, and aged, *i.e.* placed in heaps to ferment, an operation which requires great care. The glucoside is decomposed, liberating hæmatoxylin, and at the same time a large part of the hæmatoxylin is oxidized in the air to hæmatin, the active coloring principle. When sufficiently aged, the wood is ready for use.

Logwood extracts are prepared by extracting the wood with hot water and evaporating the solution under reduced pressure at a temperature not too high. The wood is extracted a second and a third time, yielding inferior grades of extract.

Composition. — The wood contains woody fiber, water, mineral matter, hæmatin, hæmatoxylin, and other substances. It varies in composition.

The extracts contain hæmatin and hæmatoxylin in an impure form. They are sometimes adulterated with glucose, molasses, chestnut extract, and other substances.

Properties. — Logwood chips or raspings appear as red, woody substances. The extract is a thick liquid, or paste. A decoction of logwood, or a solution of the extract, has a color ranging from orange-yellow to a dark reddish brown, according to the strength of the solution. The color is removed by zinc and acetic acid.

Salts. — Both hæmatin and hæmatoxylin are acids, and form salts with bases. The reactions of a decoction of logwood are due to the simultaneous presence of both hæmatin and hæmatoxylin.

The salts of lead, iron, copper, tin, silver, and some others with hæmatin are not soluble in water, and are precipitated as colored precipitates when any salts of these metals, in solution, are added to a solution of logwood.

Action to Fibers. — Logwood as a direct dye produces a reddish brown color of no practical value.

Experiment 25. — Boil a cotton skein with 30 per cent logwood extract in 200 cc. water for half an hour. Squeeze, remove a sample for your scrap-book, and save the dye-bath and remainder of yarn for Experiments 26 and 27.

Treat a skein of wool in the same way, using 10 per cent logwood extract.

Which skein is colored darker? Is either dye-bath exhausted?

Combined with iron, aluminium, chromium, or copper, logwood produces valuable dyes of different colors. That is to say, it requires metallic mordants.

Experiment 26. — (*a*) Work the cotton skein obtained in the preceding experiment 10 minutes in a cold bath of 7 per cent potassium bichromate and 5 per cent copper sulphate in 200 cc. water. The color produced is due to the oxidation of the hæmatoxylin to hæmatin by potassium bichromate, and combination of hæmatin with the metals to form a mixture of copper and chromium hæmatates.

(*b*) Boil the wool obtained in Experiment 25 with 5 per cent ferrous sulphate and 1 per cent copper sulphate in 200 cc. water for half an hour. In this case copper hæmatate and ferrous hæmatate are formed, and the latter is probably oxidized to ferric hæmatate by the air.

Wool has enough affinity for the coloring principle of logwood to absorb sufficient of it to produce a good color when afterward mordanted. Cotton, even from the strong solution used, absorbs only enough logwood to fix the mordant; for a good color, a second dyeing is necessary.

Experiment 27. — Boil the cotton mordanted in Experiment 26 with the dye-bath saved from Experiment 25. A good black is produced. Test fastness to washing.

Behavior of Fibers to Mordants. — Two classes of mordants are used in dyeing: —

(1) *Acid mordants*, such as tannic acid, or Turkey-red oil, which are used to fix fuchsine and other basic dyes on cotton in the form of insoluble tannates, etc.

(2) *Basic or metallic mordants*, which combine with dyes like logwood with acid properties to form highly colored lakes of iron, aluminium, etc.

The metallic mordants behave differently toward cotton or linen and wool or silk.

To mordant wool with metallic mordants it is boiled with solutions of alum, or potassium bichromate, with the addition of acids, whose function will be discussed later. The wool acts chemically upon the salts, decomposes them, and fixes the aluminium or chromium so that it cannot be washed out, and in such a form that it combines readily with logwood and similar colors to form the desired lakes.

Experiment 28. — Mordant a 5-gram skein of wool by boiling half an hour in a solution of 5 per cent alum and 3 per cent oxalic acid in 200 cc. water. Dye by boiling half an hour with 3 per cent hæmatin in 200 cc. water. Remove and wash. Is the bath exhausted? Test fastness to washing.

The wool fixes the alum in the form of a basic salt, leaving part of the acid in solution; it is afterward dyed blue by combination of the aluminium with the coloring principle of logwood.

Cotton is chemically less active than wool, and cannot decompose salts such as alum. It can decompose basic salts and fix them feebly.

Experiment 29. — Prepare a mordanting bath of basic aluminium sulphate (see Exp. 23) by dissolving 10 per cent alum and 2 per cent sodium carbonate in 200 cc. water, and work a boiled-off cotton skein in the solution 15 minutes. Wring out and dye without washing as described in Experiment 28.

The method illustrated by Experiment 29 is of no practical value for dyeing with logwood. Metallic mordants are fixed upon cotton by the production of insoluble compounds. Two methods of fixing iron for logwood dyeing are illustrated by Experiments 30 and 31.

Experiment 30. — Work a boiled-off skein of cotton yarn 10 minutes in a solution of 50 per cent ferric sulphate in 100 cc. water. Squeeze well, and pass through lime-water, which precipitates ferric hydroxide: —

$$Fe_2(SO_4)_3 + 3\,Ca(OH)_2 = 2\,Fe(OH)_3 + 3\,CaSO_4.$$

Dye with 10 per cent logwood extract in 200 cc. water, boiling half an hour. The cotton is dyed black.

Experiment 31. — Boil two 10-gram skeins of cotton yarn with 10 per cent sumac extract (which contains tannic acid) in 200 cc. water, until thoroughly wetted out, and allow to stand in the solution over night. Then squeeze and work 15 minutes in a bath of 15 per cent ferric sulphate in 200 cc. water; iron tannate is formed. Squeeze and work 10 minutes in 100 cc. lime-water. The excess of iron salt on the fiber is decomposed with the production of ferric hydroxide. Wash well, remove a sample, and dye with 10 per cent logwood extract in 200 cc. water, boiling half an hour. Remove and wash. One skein is saved for Experiment 34.

In the first case, the fiber is saturated with a strong solution of a ferric salt, and the salt dissolved in the water adhering to the fiber is decomposed with lime-water.

In the second case, the metallic mordant is fixed by means of tannic acid, which has some affinity for cotton, and also unites with the metal.

In both cases the cotton is dyed black by the logwood.

Polygenetic Colors. — The color produced by logwood depends upon the mordant used with it and the way in which it is applied. With aluminium (Exps. 28 and 29) the color is blue; with iron (Exps. 30 and 31), black; with potassium bichromate and oxalic acid, a shade of blue; with potassium bichromate and sulphuric acid, black.

Experiment 32. — Mordant a 5-gram skein of woolen yarn with 3 per cent sodium bichromate and 2 per cent oxalic acid in 200 cc. water, boiling half an hour. Remove a sample and boil the remainder half an hour with 3 per cent hæmatin in 200 cc. water.

Mordant a second skein as directed above with 3 per cent sodium bichromate and $1\frac{1}{4}$ per cent sulphuric acid. Remove a sample and dye with 7 per cent hæmatin.

Dyestuffs from which more than one color can be produced by the use of different mordants, are called *polygenetic* colors. *Monogenetic* colors are those which yield only one color, or shade of that color, no matter what mordant may be used.

Assistants for Metallic Mordants. — Different results were obtained in the preceding experiment, according as sulphuric acid or oxalic acid were used as assistants with potassium bichromate. The results are explained as follows: —

(1) *Sulphuric acid* liberates chromic acid from the potassium bichromate, which is taken up by the fiber: —

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2\,CrO_3 + H_2O.$$

The chromic acid is partly reduced by the wool fiber; the unreduced chromic acid oxidizes the coloring principle of logwood and then combines with it to form a black lake.

(2) *Oxalic acid* slowly produces chromium hydroxide, which is taken up by the fiber: —

$$3\,H_2C_2O_4 + 2\,K_2Cr_2O_7 = 2\,K_2CrO_4 + 2\,Cr(OH)_3 + 6\,CO_2.$$

The chromium hydroxide combines directly with the logwood without oxidation. Cream of tartar (potassium bitartrate) and lactic acid, which are also used, have the same effect as oxalic acid. Besides influencing the composition of the body absorbed by the wool, assistants are used with metallic mordants for the following purposes: —

(1) To prevent superficial and uneven mordanting. For example, wool decomposes alum so rapidly that, in mordanting in large quantities, where portions of the material

are more exposed for a time to the action of the mordanting liquid than other portions, some parts of the wool will take up the aluminium more rapidly than others, and stripes or spots will appear when dyeing. Further, the mordant is liable to be superficially attached to the wool, and the color lake subsequently formed will rub off. The addition of sulphuric acid, oxalic acid, or potassium bitartrate to the mordant bath prevents the alum from decomposing so rapidly, and aids to produce even and fast colors.

(2) To cause more of the mordant to be taken up. Sulphuric acid added to potassium bichromate, by liberating chromic acid, causes the wool to combine with a larger portion of the mordant. Wool takes up chromic acid from potassium bichromate to a certain extent: —

$$K_2Cr_2O_7 = K_2CrO_4 + CrO_3.$$

It has little action upon potassium chromate.

Methods for Dyeing with Logwood. — The methods used for dyeing with logwood and other mordant colors are as follows: —

(1) *Dyeing and mordanting* (see Exps. 25 and 26). This method is used on wool to a certain extent, hardly ever on cotton.

(2) *Mordanting and dyeing* (see Exps. 28, 29, 30, 31, and 32). The usual method for dyeing with mordant colors.

(3) *Single-bath method.* Dye and mordant are applied in the same bath. The color lake is formed and slowly absorbed after the manner of a direct dye. The method has two disadvantages: part of the color lake is liable to be fixed only superficially on the fiber, and to rub off; and part of the dye is precipitated as a lake in the bath, and lost.

Experiment 33. — Dissolve 10 per cent logwood extract, 4 per cent copper sulphate, 3 per cent sodium carbonate, and 2 per cent ammonium chloride in 200 cc. water. Enter a 10-gram skein of boiled-off yarn, heat to boiling, and boil half an hour. Remove and wash. Test fastness to washing.

The single-bath method is, however, largely used both for cotton and wool, especially in the case of cheap dyes like logwood, in which the cost of the dye is not great compared with the cost of time and labor in dyeing.

Saddening. — Cotton or wool mordanted and then dyed with logwood retains an excess of the coloring matter held somewhat loosely. Where a high degree of fastness is required, the excess is fixed or made insoluble by a second mordant bath. The operation is called *saddening*.

Experiment 34. — Sadden one of the skeins dyed in Experiment 31 by working 15 minutes in a bath of 1 per cent copperas in 200 cc. water. Compare fastness of the saddened and not saddened skeins to washing and boiling water.

Soaping. — The appearance of cotton dyed with logwood is improved by *soaping*. Soaping often follows dyeing, to remove coloring matter held only loosely by the fiber, and to soften the material.

Experiment 35. — Work a skein of cotton yarn dyed black with logwood for 15 minutes in a solution of 4 per cent soap in 200 cc. water heated to 60° C. Dry without washing.

Application of Logwood. — Large quantities of logwood are used for producing blacks upon cotton and wool. It is also used, to a slight extent, for other colors on wool.

The color, properly dyed, possesses a high degree of fastness to light, washing, and acids. If not properly dyed, the color is liable to *rub off;* it is not fast to rubbing.

Experiment 36. — Test the fastness of the dyeings obtained in Experiments 28, 30, 32, and 33 to washing, acids, and alkalies. Test fastness to rubbing of all dyeings with logwood as follows: —

Rub vigorously on a piece of white paper or cloth. If the material is stained, the color is not fast to rubbing.

Mordant Colors. — Logwood is a representative of the mordant colors. These are dyestuffs which are invariably fixed upon the fiber in the form of metallic lakes, with a color which may be different from that of the coloring principle. There is considerable variation in the properties of the mordant colors. They are very important dyes, being characterized by great fastness to washing, light, and other agencies.

CHAPTER VI

INDIGO — CHROME-YELLOW

INDIGO is a valuable blue dye, which has been in use for ages. It is prepared from varieties of Indigofera, a plant of the bean family, grown chiefly in India. Indigo is also contained in woad, a plant formerly grown in Europe, but now almost entirely replaced by indigo. In recent years indigo has been prepared artificially.

Preparation. — Indigo (like the coloring principle of logwood) exists in the indigo plant and in woad in the form of a glucoside, indican, which is decomposed by acids into a sugar, and the coloring principle, indigotin. To separate indigo, the stems and leaves of the plant are covered with water, and allowed to ferment. The indican is decomposed and the sugar destroyed, while the indigo is reduced to indigo-white, and dissolves. The liquid is drawn off and stirred and splashed by workmen, to expose it to the air. The yellow liquid assumes a greenish color, and indigo separates in flakes. It is allowed to settle, and is washed several times, and finally boiled with water to prevent further fermentation. It is then collected and dried.

Composition. — Natural indigo, besides the blue coloring principle, indigo blue, or indigotin, contains small quantities of other coloring matters and other impurities. Its composition is as follows: —

Indigotin	20 to 80 per cent.
Indigo-red	3 to 5 per cent.
Indigo-gluten	2 to 5 per cent.
Indigo-brown	1 to 6 per cent.
Water	3 to 8 per cent.
Ash	3 to 10 per cent.

The average content of indigotin is 45 per cent.

The amount of ash in inferior grades of indigo may be as high as 35 per cent.

Artificial Indigo. — In 1885 A. Baeyer discovered a method of preparing indigo-blue, or indigotin. Other methods have since been devised. At present, large quantities of synthetic indigo are manufactured, and the competition between the natural and the artificial product is sharp.

Properties. — Commercial indigo appears as dark blue cakes, sometimes as a powder. Artificial indigo is sometimes sold in the form of indigo-white. Indigo is insoluble in water, dilute acids, or alkalies. It is soluble in boiling alcohol, with a blue color, but is deposited again on cooling.

Nitric acid, chromic acid, and other strong oxidizing agents destroy indigo with the production of colorless or yellow bodies. Concentrated sulphuric acid dissolves it, forming a new dye soluble in water.

Experiment 37. — Boil a small quantity of indigo with a little water in a test-tube, and filter the hot liquid. Repeat, using dilute hydrochloric acid. Does the indigo dissolve?

Heat a little indigo in a test-tube with dilute nitric acid. What happens?

Reduced Indigo. — Like all other dyes, indigo is reduced and decolorized by reducing agents. It yields a leuco body known as indigo-white.

$$\underset{\text{Indigo.}}{C_{16}H_{10}N_2O_2} + 2\,H = \underset{\text{Indigo-white.}}{C_{16}H_{12}N_2O_2}.$$

Reduced indigo, or indigo-white from natural indigo, consists of the leuco compounds of indigotin with small quantities of reduced indigo-red. It is a grayish white body, insoluble in water and dilute acids, but as it has acid properties, it unites with bases, such as sodium hydroxide or slaked lime, to form salts. The sodium and calcium salts are soluble in water. On exposure to the air, indigo-white is rapidly oxidized to indigotin; the yellowish solution becomes first green, then blue, and is then covered with a scum consisting of minute crystals of indigo.

Dyeing with Indigo. — Indigo is applied in the form of the calcium or sodium salt of indigo-white, and oxidized to indigo by exposure to the air. The indigo is thus produced in an insoluble form upon the fiber. The reduction of indigo is effected by several processes, which will be described below. The depth of color obtained with an indigo vat depends on: —

(1) The strength of the solution, *i.e.* the quantity of indigo-white contained in the liquid which saturates the fiber.

(2) The number of times the material is immersed in the liquid, or "dips," as it is called. "One dip" indigo is a light color. Four dips is rarely exceeded for even the deepest shades.

The methods of reducing indigo are four, as follows: —

(1) *Copperas Vat.* — The reducing agent is ferrous hydroxide. The vat consists of a mixture of copperas (ferrous sulphate), slaked lime, indigo, and water.

The copperas and slaked lime react as follows: —

$$FeSO_4 + Ca(OH)_2 = Fe(OH)_2 + CaSO_4.$$

The ferrous hydroxide then reduces the indigo: —

$$2\,Fe(OH)_2 + 2\,H_2O + I = 2\,Fe(OH)_3 + IH_2.$$

The indigo-white dissolves in the excess of slaked lime, and the ferric hydroxide settles to the bottom of the vat. It is likely to contain some indigo, which can be recovered by dissolving the sediment in an acid when the vat is let off.

The copperas vat is used for cotton only.

Experiment 38. — Grind 3 g. indigo to a thin paste with a little water, and dilute to 500 cc. Add 8 g. copperas, and when dissolved place the liquid in a tall beaker or cylinder. Then add 10 g. lime, slaked, and ground to a paste with a little water. Allow the precipitate to settle. Saturate a boiled-off skein of cotton yarn in the liquid by turning it beneath the surface of the liquid for a few minutes. Take it out and observe any change in color. Give another skein of yarn three dips, exposing it to the air between each dip.

(2) *Hyposulphite or Hydrosulphite Vat.* — In this vat the reducing agent is sodium acid hyposulphite ($NaHSO_2$).

The first step is the preparation of sodium hyposulphite, by the action of zinc dust in a strong solution of sodium acid sulphite: —

$$3\,NaHSO_3 + Zn = NaHSO_2 + ZnNa_2(SO_3)_2 + H_2O.$$

Zinc-sodium sulphite crystallizes from the warm solution.

This solution is poured into a warm mixture of water, indigo ground to an impalpable paste, and slaked lime. Reduced indigo is formed, which dissolves in the calcium hydroxide: —

$$NaHSO_2 + I + H_2O = NaHSO_3 + IH_2.$$

The hyposulphite vat does not take long to prepare. It is used for cotton and wool.

Sodium acid hyposulphite is very unstable; in the air it oxidizes rapidly to sodium sulphite, and in closed vessels it changes to sodium thiosulphate: —

$$\underset{\text{Acid sodium hyposulphite.}}{2\,NaHSO_2} = \underset{\text{Sodium thiosulphate.}}{Na_2S_2O_3} + H_2O.$$

For this reason the substance is prepared only when it is to be used at once.

(3) *Zinc Vat.* — The vat is made up with zinc, indigo, water, and lime.

$$Zn + I + 2\,H_2O = IH_2 + Zn(OH)_2.$$

(4) *The Fermentation Vat.* — In this vat the indigo is reduced by the fermentation of bran, starch, molasses, or similar substances, and the indigo-white formed is dissolved by the addition of slaked lime. It is largely used in wool dyeing.

Fastness of Indigo. — Dyeings of indigo are very fast to washings, acids, alkalies, and light. It is liable to rub, especially so when not properly applied.

EXPERIMENT 39. — Test the fastness of the indigo dyeings (Exp. 38) to washing, acids, alkalies, and rubbing.

Indigo Extract. — Sulphuric acid dissolves indigo and changes it chemically. When its action is continued long enough, an acid is formed which is soluble in water, forms salts with bases, dyes wool directly in an acid bath, and in general has properties similar to Biebrich scarlet. The product is an acid dye. It is prepared in several degrees of purity, and is known as acid indigo extract, neutral extract of indigo, refined extract, best refined extract, and soluble indigo. Indigo extract is not applicable to cotton; and on wool it is not as fast to washing and light as indigo.

Chrome-yellow. — Chrome-yellow is a mineral color, being lead chromate ($PbCrO_4$). It is produced by chemical action directly upon the fiber. Lead chromate is precipitated when a solution of a lead salt and a chromate or bichromate are brought together: —

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2\,KNO_3.$$

Lead chromate is insoluble in water; it is soluble in nitric acid, and is decomposed by a hot solution of sodium or calcium hydroxide, forming an orange compound known as chrome-orange: —

$$2\,PbCrO_4 + Ca(OH)_2 = Pb_2CrO_5 + CaCrO_4 + H_2O.$$

Continued action of lime-water effects complete decomposition.

Production. — Chrome-yellow is dyed on cotton only. Two methods may be used: —

(1) The cotton is impregnated with a solution of lead acetate or lead nitrate, and passed through lime-water to precipitate lead hydroxide: —

$$Pb(NO_3)_2 + Ca(OH)_2 = Pb(OH)_2 + Ca(NO_3)_2.$$

Lead chromate is then formed by passing the material through a solution of potassium or sodium bichromate.

(2) The cotton is worked in a solution of sodium plumbite, prepared by the action of an excess of sodium hydroxide on a lead salt: —

$$Pb(NO_3)_2 + 4\,NaOH = Na_2PbO_2 + 2\,NaNO_3 + 2\,H_2O.$$

The cotton probably absorbs lead hydroxide from this solution. An acidulated solution of potassium bichromate develops the color. Zinc sulphate may be used in place of the acid.

EXPERIMENT 40. — Dissolve 2 per cent lead acetate and 16 per cent sodium hydroxide in 200 cc. water. Sodium plumbite (Na_2PbO_2) is formed. Write reaction.

Work a skein of boiled-off cotton yarn 10 minutes in this, squeeze well, and work 5 minutes in a bath of 15 per cent potassium bichromate and 2 per cent zinc sulphate in 200 cc. water. Reaction? Wring, wash, and dry. Test fastness to acids, alkalies, washing, and rubbing.

The baths used in this experiment are not exhausted, and are used continuously, being freshened up from time to time by additions of the reagents.

Properties. — The color is very fast to light, acids, and washing. It adds to the weight of the cotton, sometimes as much as 40 per cent. Lead chromate is poisonous, and injurious to the health of people who handle dry yarn dyed with it, on account of the dust rubbed from it. Improperly dyed, lead chromate rubs badly. Combined with indigo, it produces a fast green.

Retrospect. — We have now studied representatives of the different classes of dyes, namely: —

(1) *Direct cotton colors*, which are direct colors for all materials. They are salts of color acids, and are dyed in the form of salts.

(2) *Basic dyes*, which are direct dyes for animal fibers, and are fixed on cotton by means of tannic acid. They are salts of color bases, and are dyed in the form of salts.

(3) *Acid dyes*, which are direct dyes for animal fibers, and cannot be fixed firmly on cotton. They are salts of color acids, and are dyed in the form of acids, on wool and silk.

(4) *Mordant dyes*, which are dyed as metallic salts of aluminium, chromium, etc. They are weak acids, or salts, and are combined with the metals on the fiber.

(5) *Insoluble dyes*, which are produced in an insoluble form upon the fiber.

The above division is based on practical requirements, and for convenience in study. There is no sharp line of demarcation between all the different groups; the acid colors and the mordant colors are frequently related to each other, and so are the acid colors and the direct cotton colors. It is sometimes difficult to say to which group a dyestuff belongs.

Theory of Dyeing. — The theories of dyeing explain the action of direct dyes, in which the dyeing is a result of the attraction of fiber for dyestuff. When mordants are used, the force which comes into play in dyeing is the chemical attraction between dyestuff and mordant, which is largely independent of the fiber.

Two theories have been advanced to explain the nature of dyeing.

(1) The *mechanical theory* explains dyeing as a purely physical process. The fibers are solid solvents, and the dyestuff distributes itself between dye-bath and fiber according to its solubility in the two solvents. The operation is analogous to the extraction of a substance from water by ether; such as eosine, for example.

EXPERIMENT 41. — Dissolve a little eosine in water, and shake the solution in a test-tube with a little ether. The ether dissolves part of the eosine, and becomes colored. Add a few drops of hydrochloric acid, and shake again. The ether extracts nearly all the dye, and the water becomes almost colorless.

(2) The *chemical theory* supposes dyeing to be due to chemical combination between dyestuff and some constituents of the fiber, the resulting compound being held in a state of solid solution.

The nature of dyeing really depends upon the fiber which is dyed.

Cotton. — In dyeing cotton with direct cotton colors, the fiber probably acts as a solvent and extracts the dye from the bath because it is more soluble in cotton than in the dye liquid. When the dyed cotton is boiled with water, the color again distributes itself according to its relative solubility in the two solvents. The behavior of cotton to tannic acid and other mordants is explained in the same way.

Wool and Silk. — In the case of the animal fibers, dyeing is probably due to the formation of chemical compounds. The following facts support this statement: —

(1) If wool is dyed with a basic color, such as fuchsine, the whole of the hydrochloric acid remains in solution as evidence of chemical action.

(2) Wool boiled with a solution of the colorless base of fuchsine is dyed red, evidence of the formation of a salt.

(3) Alcohol extracts the color from silk or wool dyed with night blue (a basic color), and a lake is precipitated on the addition of water. The lake contains the dye combined with an acid constituent of the fiber. Separated from the dye, this substance precipitates fuchsine from solution, as a lake which is soluble in alcohol.

The *mordanting* of silk and wool seems due to chemical action likewise.

Classes of Fibers. — We have seen that cotton and wool behave very differently towards dyes and mordants. Wool has a great affinity for most dyes, absorbs them readily, and holds them with tenacity. Wool decomposes mordants readily and easily, and retains them with considerable force. Cotton is inactive; it has little affinity for most dyes, and for mordants it has little attraction also. These differences in the behavior of wool and cotton are characteristic of the two classes of fibers, the animal fibers acting like wool, and the vegetable fibers like cotton.

CHAPTER VII

VEGETABLE FIBERS — COTTON

VEGETABLE fibers may be divided into two groups: —

(1) *Seed hairs;* that is, fibers attached to the seed of plants, — as the common thistle, dandelion, and cotton. Cotton is the only fiber of this kind of commercial importance. Each fiber is composed of a single cell. They vary from one-fourth to two inches in length.

(2) *Bast fibers;* fibers from the stem or leaves of plants, — as jute, flax, etc. The fibers may be quite long, in some cases upward of six feet. They are compound fibers, being composed of bundles of cells cemented together. The cells or ultimate fibers are quite short.

About thirty kinds of vegetable fibers are used in the United States, not all of them, however, as textile fibers. The most important are cotton, flax (linen), hemp, jute, and China grass.

Cotton. — Cotton consists of the seed hairs of various species of Gossypium. About two-thirds of the world's supply of cotton comes from the United States. The remainder comes mostly from India, the East Indies, Brazil, and Egypt. The United States manufactures 27 per cent of the cotton it produces, — the Southern States one-third of this.

Cotton is inclosed in a three- to five-valved capsule or *boll,* which bursts when ripe. It is picked by hand, and *ginned* to remove seeds and coarse impurities, like leaves, from the seed hairs or *lint*. The cotton is packed in *bales* weighing from three to five hundred pounds.

The seeds are manufactured into valuable products, — cotton-seed oil, used as a salad oil, as a lard substitute, and in soap making; cotton-seed meal, used as a cattle food and as a fertilizer; cotton-seed hulls, used as a feed, as a fuel, and as a fertilizer.

Motes. — In ginning cotton, small particles of the seeds are often nipped off, and pass into the lint. Sometimes these are not removed during the processes of cotton manufacture, and appear on the yarn or in the woven cloth as black spots or *motes*. Under certain circumstances, motes give up oil to the fiber, which can cause unevenness in dyeing, since it acts as a mordant to basic dyes. The oil may also prevent dye from going on to the fiber.

Grades of Cotton. — Cotton is graded chiefly by its length of fiber, though its color and freedom from dust, leaves, seeds, and seed particles are also considered. The longer fibers are smaller in diameter, are silkier, and can be spun into finer threads than the coarser.

Our cotton is of two types. Sea Island cotton has the longest and finest staple, and commands the highest price of any commercial cotton. It is grown only on the islands and along the shores of South Carolina and Florida, and to a limited extent along the Gulf of Mexico, and is less than 1 per cent of our crop.

The remaining 99 per cent, known as the American Upland, has a longer staple and is of better quality than the East Indian and other growths, except the Egyptian, which comes between the American Upland and Sea Island in quality and price.

Peru produces a peculiar variety of cotton, with a strong, rough, crinkly staple known as "vegetable wool," much used by manufacturers for mixing with wool, and is difficult to detect except by chemical tests.

The following table[1] shows the average length and diameter in inches of the principal cotton fibers: —

	Length	Diameter
Sea Island	1.61	.000640
Egyptian	1.41	.000655
New Orleans	1.02	.000775
American Upland	0.93	.000763
Brazilian	1.17	.000790
Indian	0.89	.000844

The diameter of other textile fibers is as follows: —

	Diameter in inches
Silk	.00072
Linen	.00060 to .00148
Wool	.00033 to .00181

Microscopic Appearance. — Cotton fibers, under the microscope, have the appearance of irregular, flattened, and somewhat twisted tubes, tapering to a point at one end. They may be compared to a hollow twisted ribbon. The twist distinguishes cotton from all other fibers (Fig. 1).

When young, each cotton fiber consists of a single circu-

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[1] U. S. Dept. Agr., Office of Expt. Stations, *Bull.* No. 33, p. 77.

lar cell filled with a liquid. With increase in length, the cell walls become thinner, and finally collapse. After the boll bursts, the liquid contents solidify by exposure to sun and air, and the dissolved matters are deposited somewhat irregularly on different parts of the cell walls, causing the fiber to twist.

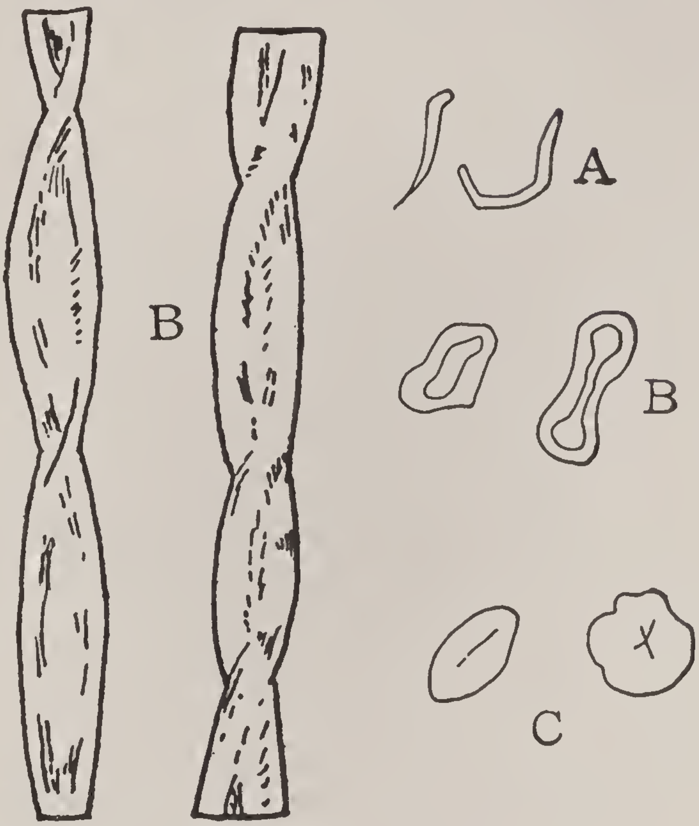

FIG. 1. — Cotton fiber.

A, unripe (section); *B*, ripe; *C*, mercerized cotton.

Dead Cotton. — Every lot of cotton contains ripe, unripe, and half-ripe cotton, due to different stages of maturity of the filaments on different parts of the same seed. In unripe cotton (Fig. 1, *A*), the fibers show no indication of tubular structure, but present the appearance of broad, solid, ribbon-like fibers which are almost transparent, and show irregular folds. Such fibers, which are technically known as "dead cotton," are difficult to dye, and may sometimes be met with as white specks in dyed cotton goods.

Other Defects. — Solid places are sometimes found in the ripe cotton fiber; and at these points the cotton has less affinity for dyestuffs than at others, so that the fiber is dyed irregularly. Only ripe, perfect cotton fibers possess all the requisites for perfect spinning and dyeing. From these statements it is seen that the physical *structure* of the cotton fiber, no less than its chemical composition, plays an important part in the process of dyeing it.

Composition. — Cotton as it comes on the market contains about 8 per cent water, 87 per cent cellulose, and 5 per cent other substances, consisting of cotton wax, cotton oil, pectic acid, coloring matters, and albuminous matters. The quantity of water in baled cotton is not subject to great variations, differing in this respect from wool and silk. The substances other than cellulose are removed, for the most part, during the process of *bleaching*, so that bleached cotton consists of almost pure cellulose.

Cotton Wax. — Cotton wax is a waxy substance, insoluble in water, but soluble in alcohol. It does not dissolve when boiled with dilute solutions of caustic soda. This wax is found fairly uniformly distributed over the surface of the cotton fiber, and it is due to this fact that raw cotton is wetted by water only with difficulty.

Fatty Acids. — These are organic acids, which form soluble salts (soap) with caustic soda.

Coloring Matters. — Two brown coloring matters are found in cotton. Egyptian cotton contains relatively large quantities of them, which accounts for its dark color. The lower grades of cotton are much darker than the finer qualities.

Pectic Acid. — This is a gum-like substance, soluble in boiling water. It is precipitated from solution by acids. Alkalies combine with it, forming brown substances, not so readily soluble in water as pectic acid itself.

Cellulose. — As stated, the greater part of the cotton fiber is composed of cellulose. Cellulose makes up a large part of all vegetable fibers, and is also found in the wood of trees, and the stems and leaves of almost all plants. Cotton is the purest natural cellulose, bleached cotton being composed of nearly pure cellulose. Paper consists of more or less pure cellulose.

With the exception of cotton and linen, all textile fibers in their commercial form contain large quantities of other substances than cellulose, so that while the properties of cotton and linen are those of pure cellulose modified to some extent on account of the structure of the fiber, the properties of other textile fibers may be different to a large extent, on account of the other bodies present.

Preparation and Properties. — Pure cellulose may be prepared from cotton by washing it with alcohol and ether, boiling it for some time with a solution of potassium hydroxide, washing well, and drying. It cannot be prepared so easily from other materials.

Cellulose contains carbon, hydrogen, and oxygen in the proportion corresponding to the formula $C_6H_{10}O_5$. $(C_6H_{10}O_5)_x$ represents a molecule of cellulose. The molecular weight of cellulose is unknown.

Cellulose belongs to a naturally occurring class of substances known as carbohydrates, of which starch, dextrin, and sugar may serve as examples. It may be converted into a sugar, $C_6H_{12}O_6$, glucose, if it is dissolved in concentrated sulphuric acid and the solution diluted and boiled.

$$\underset{\text{Cellulose.}}{(C_6H_{10}O_5)_x} + XH_2O = \underset{\text{Glucose.}}{XC_6H_{12}O_6}.$$

Cellulose is colorless, tasteless, without odor, and insoluble in water, alcohol, ether, or other ordinary solvents. It is characterized by its inactivity; methods for separating cellulose from plant tissues rest on the use of reagents which dissolve the other substances, and leave the cellulose unchanged. Its specific gravity is 1.5. When it burns freely, it does not emit any strong odor, but smoldering cotton gives off the characteristic odor of acrolein.

Solvents for Cellulose. — Solution of cellulose is invariably accompanied by chemical change, which usually consists in combination with water, or hydration. The solutions, as a rule, are unstable, with the result that cellulose can easily be precipitated from them. Cellulose is dissolved by concentrated solutions of zinc chloride, copper hydroxide in ammonia, concentrated sulphuric acid, and some other solvents.

The solution in *zinc chloride* is used for making cellulose filaments, which are carbonized for use in incandescent lamps. The solution is allowed to flow through a narrow orifice into alcohol, which precipitates a thread of hydrated cellulose mixed with zinc hydroxide. It is washed with water and acids, dried and carbonized.

EXPERIMENT 42. — Dissolve 10 g. zinc in concentrated hydrochloric acid, and evaporate to about 20 cc. under the hood. While hot, add 1 g. loose cotton, stirring carefully. What happens? Pour a portion of the solution into water; into alcohol. What is the precipitate?

Ammoniacal Copper Oxide. — This solvent may be prepared in two ways: —

(1) Copper is covered with strong ammonia, and air or oxygen passed through the mixture. The copper is oxidized, and dissolves.

$$Cu + O + H_2O = Cu(OH)_2.$$

(2) Copper hydroxide is precipitated by mixing solutions of copper sulphate, containing a little ammonia or glycerol, with sodium hydroxide. The precipitate is washed, and dissolved in strong ammonia.

$$CuSO_4 + 2\,NaOH = Cu(OH)_2 + Na_2SO_4.$$

Ammoniacal copper oxide is a blue liquid, with a strong odor of ammonia. It dissolves cellulose, forming a viscous solution. Cellulose hydrate is precipitated when the solution is poured into dilute hydrochloric acid, water, or alcohol, or when sodium chloride, potassium chloride, sugar, or some other substances are added to the solution.

The Willesden process of water-proofing consists in passing rope, canvas, or paper through an ammoniacal solution of copper hydroxide, and drying. The substance becomes coated with a film of gelatinized cellulose, mixed with copper hydroxide, of a bright green color; the pores are filled, so that water cannot penetrate it, and the copper is a protection against the attack of insects, or molds.

EXPERIMENT 43. — Dissolve 20 g. copper sulphate and 10 cc. glycerol in 1000 cc. water, and add a dilute solution of sodium hydroxide until the liquid is faintly alkaline. (Reaction?) Allow the precipitate to settle, which may take several hours, pour off the clear liquid, and filter out the precipitate on a large filter. Allow it to drain well, and add the precipitate to 30 cc. of ammonia 0.90 sp. gr. until no more dissolves. Immerse a piece of cotton cloth in the liquid, remove, and dry without washing. Describe its properties. Add some cotton wool to the solution, and stir well. Does it dissolve? Pour a portion of the solution into water.

Concentrated Sulphuric Acid. — Concentrated sulphuric acid first causes cellulose to swell, forming a gelatinous mass, and if this is rapidly diluted with water, a substance termed amyloid is precipitated.

Vegetable parchment is prepared by precipitating amyloid upon ordinary unsized paper, which consists mostly of cellulose. The paper is placed a few seconds in acid of the proper strength, then washed thoroughly. The product is a tough, translucent paper. Other solvents for cellulose, as zinc chloride, or phosphoric acid, act in the same way.

Cellulose dissolves completely in strong sulphuric acid in a short time, cellulose sulphates being formed. If the solution is diluted with water and boiled for some time, the cellulose is converted into glucose.

Cellulose treated with caustic soda, and then with carbon bisulphide, dissolves, but in time the solution decomposes and forms a jelly which may absorb large quantities of water without becoming liquid. The compound is called cellulose thiocarbonate, and has been proposed for use in the production of artificial silk. The solution (called *viscose*) is used for sizing paper, and has other uses.

Cellulose Nitrates. — When cellulose is brought in contact with nitric acid at a low temperature, cellulose nitrates are formed. The extent of the nitration depends on the concentration of the acid, etc.

Cellulose tetra-nitrate, $C_{12}H_{16}O_6(ONO_2)_4$, and the penta-nitrate, $C_{12}H_{15}O_5(ONO_2)_5$, are formed when cellulose is treated for a short time with a mixture of nitric and sulphuric acids.

$$(C_6H_{10}O_5)_2 + 4\,HNO_3 = C_{12}H_{16}O_6(ONO_2)_4 + 4\,H_2O.$$

They are soluble in a mixture of alcohol and ether, and the solution, known as collodion, used in photography. When poured upon any surface, such as glass, the ether and alcohol evaporate rapidly, leaving a thin coating of nitrates, which is sensitized by the photographer. The solution is also used in the preparation of *artificial silk* (Chapter XX).

Cellulose hexa-nitrate, $C_{12}H_{14}O_4(ONO_2)_6$, is made by treating cellulose with a mixture of nitric and sulphuric acids for twenty-four hours at 10° C. Prepared from cotton, it is known as *guncotton*, and is used as an explosive and in the preparation of smokeless powders.

Celluloid is a mixture of guncotton and camphor, prepared by compressing the two with the addition of alcohol. It is hard and brittle when cold, but at a slightly elevated temperature it can be molded into any shape desired. It is very inflammable.

Oxycellulose. — Cellulose offers a comparatively great resistance to oxidizing agents, most of the reagents for purifying (bleaching) or isolating cellulose being oxidizing agents which readily attack the other substances with which it is mixed in the raw condition. On the other hand, cellulose is oxidized by nitric acid, potassium permanganate, chromic acid, bleaching powder, and even the air under suitable conditions, oxycelluloses being formed.

The appearance of the cellulose depends on the extent of the oxidation; a moderate oxidation does not cause the fiber to lose its shape, or affect its strength to any great extent, but vigorous oxidation causes it to crumble. Some of the oxycelluloses are partly soluble in alkalies.

Under certain conditions, the production of oxycellulose is the cause of defects in bleaching. Oxycellulose may be detected by the aid of certain dyes; some, as methylene blue or methyl violet, have a greater affinity for oxycellulose than for cellulose; with others, the reverse is the case.

Experiment 44. — (1) Mix 2 g. bleaching powder, in a mortar, to a paste with 10 cc. water, and place a spot about the size of a five-cent piece on a piece of cotton cloth about 4 in. square. After standing half an hour, wash with water, then with water acidulated with hydrochloric acid, and with water made slightly alkaline with ammonia, and proceed to dye as in (3).

(2) Mix 2 g. potassium bichromate and about $\frac{1}{2}$ cc. sulphuric acid with 10 cc. water, and proceed with it as directed for the paste above.

(3) Dye both pieces of cloth by boiling with $\frac{1}{2}$ per cent (of 10-gram) methylene blue in 200 cc. water. Wash well, dry, and enter material in scrap-book.

What can you say of the behavior of methylene blue toward cellulose and oxycellulose? Methylene blue is a basic dye.

Action of Acids. — Dilute mineral acids, as sulphuric, or hydrochloric, have little action upon cellulose, unless allowed to dry upon it; as the fiber dries, and the acid becomes more and more concentrated, the cellulose is affected. Fibers composed of cellulose, like cotton or linen, become weaker under such conditions, or fall to a powder, according to the conditions. The degree to which this change occurs depends on the temperature at which the drying takes place, and on the strength of the acid. Quick drying at a high temperature has a much more vigorous action than slow drying. If the acid is taken strong enough, the cellulose is completely disintegrated, and falls to a powder which has the composition $C_{12}H_{20}O_{10} . H_2O$ and is called *hydro-cellulose.*

The same effect is produced by magnesium chloride, aluminium chloride, or ferric chloride, which decompose on drying, with the production of hydrochloric acid: —

$$AlCl_3 + 3\,H_2O = Al(OH)_3 + 3\,HCl.$$

Carbonization. — The destruction of vegetable fibers by the action of mineral acids at an elevated temperature is called carbonization, for the reason that the hydro-cellulose is usually black, or nearly so, and it was thought to be carbon. Wool is not destroyed under the conditions of carbonization. The applications of carbonization are: —

(1) To remove burs from wool, and cotton or linen from woolen rags. The rags are immersed in a mineral acid, and dried at a suitable temperature, or they are heated, and hydrochloric acid gas passed over them. Afterward, the hydro-cellulose dust is beaten out, and the wool remanufactured.

(2) To produce gauze patterns in mixed cotton-wool goods. A design is printed upon them with a thickened solution of aluminium chloride, and they are dried at the proper temperature, when the cotton is destroyed, leaving the wool.

EXPERIMENT 45. — Dilute 4 cc. conc. sulphuric acid to 100 cc., soak in it a piece of cotton goods, a piece of wool, and a piece of mixed cotton and wool. Dry at a temperature above 80°, and explain results.

Action of Alkalies. — Cellulose has weak acid and basic properties, and will absorb acids or alkalies from very dilute solutions. Beyond this, dilute solutions of caustic alkalies have no action on cotton, whether hot or cold, and the same may be said of sodium or potassium carbonate, soap, borax, and phosphate of soda.

Mercerization. — When cotton is treated with strong solutions of caustic soda and washed, it undergoes a peculiar change. It contracts 20 to 25 per cent in length, and becomes heavier, denser, and stronger. This change was first observed in 1850 by John Mercer, an English cotton printer, from whence it has the name, *mercerization.*

Nature of the Change. — The cellulose first combines with caustic soda, forming a compound of the composition: —

$$C_{12}H_{20}O_{10} . 2\,NaOH.$$

Washed with water, this decomposes with the production of cellulose hydrate, $C_{12}H_{20}O_{10} . H_2O$, which is the formula of mercerized cotton; the gain in weight of the cotton is 4.5 to 5.5 per cent.

The structure of the fiber also changes. A microscopic examination (Fig. I, *C*) shows that the cell walls have become thicker, the central opening has decreased in size, and the general shape of the fiber has changed from the form of a collapsed tube to that of a round, rod-like shape. It has also received a peculiar spiral twist, which explains its shrinkage, by a process of drawing-in.

Properties. — Mercerized cotton differs from ordinary cotton in several respects. It has a much greater affinity for dyes, especially for direct cotton colors like congo red, taking up more from solution, and leaving less in the dye-bath.

Mercerized cotton has also a greater affinity for *mordants* than ordinary cotton. It takes up 40 per cent of tannic acid when the latter takes up only 20 per cent under the same conditions.

EXPERIMENT 46. — Dissolve 80 g. caustic soda in 400 cc. water, and allow the solution to cool. Don't get it on your hands.

Cut a piece of unbleached cotton cloth about six inches long and two inches wide, measure it carefully, wet it and squeeze, then immerse it 5 minutes in the above solution, remove, wash, and dry. Remeasure. How much has it shrunk? What per cent?

Immerse 4 boiled-off skeins of cotton yarn in the solution, work carefully for 5 minutes, remove, wash with water, and with water containing a little acetic acid, and dry. Save them for Experiment 47. Are they in any way different from ordinary cotton?

EXPERIMENT 47. — Dye a skein of mercerized cotton with $\frac{1}{2}$ per cent diamine blue BX and 10 per cent sodium sulphate in 200 cc. water, boiling 15 minutes. Is the bath exhausted? This dye is a direct cotton color.

Dye an unmercerized skein in the same way. Which skein takes up the more dye? Which is darker?

Test fastness to acids, alkalies, and washing. Is the color faster on mercerized or on unmercerized cotton?

EXPERIMENT 48. — (*a*) Work a skein of mercerized cotton 30 minutes in 2 per cent tannic acid in 200 cc. cold water.

Mordant an unmercerized skein (boiled-off) in the same way.

Dye each in a separate bath of $\frac{1}{2}$ per cent methyl violet in 200 cc. of water, at 50° C., working 20 minutes. Is the bath exhausted? Which skein takes up the more dye? The depth of color depends on the amount of tannic acid taken up. Which takes up the more tannic acid?

Test fastness to acids, alkalies, and washing. Is the color faster on mercerized or unmercerized cotton?

(*b*) Dye a skein of mercerized cotton with ½ per cent methylene blue in 200 cc. water, at 50° C., working 15 minutes.

Dye an unmercerized skein in the same way. What difference do you see?

Both of these dyes are basic colors.

Mercerized cotton is said actually to require less dyestuff fixed upon it to produce the same shade, than other cotton. The saving in dye may be 10 to 15 per cent for light shades, 25 to 30 per cent for dark ones. The cause of this may be that the color is absorbed in the outer surface of the mercerized fiber, without penetrating to any extent in the canal, since the fiber is practically solid.

Mercerized cotton has important applications which will be treated in a later chapter (Chapter XX).

Tendering of Cotton. — When a fiber is weakened by anything which may come in contact with it during the ordinary process of manufacture, as in bleaching, dyeing, etc., it is said to be *tendered*. The tendering may take place only to a slight extent, or it may result in an actual destruction of the fiber. Tendered goods are found to be "rotten" after a short time. The following agencies may tender cotton: —

Mildew. — Mildew is a plant, which requires warmth, water, and food before it can grow. Bleached cotton is not likely to mildew, as it contains no food for the organism. Dry cotton will not mildew, but in a warm, damp atmosphere it is liable to mildew, especially goods which have been starched, or stiffened with gum or other vegetable matters, as is usually the case with finished calicoes. The starch or gum is a good food for the mildew. Mildew can easily be removed by bleaching, though the tenacity of the fiber is somewhat impaired.

Frost. — Wet cotton, exposed to a freezing temperature, is liable to damage. The water sucked into the canal of the fiber by capillary attraction, expands with great force, and bursts the fiber asunder.

Crystals of Salts. — If crystals are allowed to form in the canal of the cotton fiber, it may be weakened. The cell walls are penetrated and cut by the sharp edges of the crystals when they are closed in upon them by any strain. Crystals may be formed in the fiber when cotton is treated with solutions containing large quantities of salts of any kind, and allowed to dry without washing.

Acids. — Whenever mineral acids come in contact with cotton, it afterwards must be washed thoroughly, since they will tender the fiber if allowed to dry upon it.

Acetic acid has no action on cotton, nor has oxalic, tartaric or citric acids under ordinary conditions, but the last three may tender cotton at a high temperature, as when steamed with it under pressure. Cotton is steamed under pressure sometimes when it is printed, and as these acids are used in printing, there is danger of damage.

Salts, as aluminium chloride, ferric chloride, and magnesium chloride, which decompose with the formation of free acids, will tender cotton if dried upon it.

Oxidation. — The cotton fiber is liable to be tendered by oxidation during processes of bleaching and dyeing. Damages by oxidation during bleaching are discussed in Chapter XI.

Cotton Manufacture. — Loose cotton passes first to the *opener*, where it is subjected to the action of a beater, and a blast of air, which partially cleans it, and separates its matted flakes. It then goes to the *lapper*, which cleans it further, from which it comes out as flat sheets, which are rolled up into *laps*.

The cotton passes from the lapper to other machines which clean it further, then to machinery which cards it with wire teeth, so that the fibers are laid parallel. It is then formed into a loose, continuous strand called a *sliver*, which is drawn, and finally twisted into yarn, passing through a number of machines.

Yarn is wound, as spun, on wooden bobbins, or on a hollow pasteboard tube, in which form it is called the *cop*. In the cop, the threads are wound tightly one on the other, forming a solid, compact spindle, with a hollow core.

In forming skeins, a single cop or bobbin is wound off in a circular form, from 54 to 72 in. in circumference. A skein is composed of a single, continuous thread. In forming warps, from 50 to 1000 or more cops are wound off together, producing a bundle of parallel strands, sometimes several thousand yards long.

The warps and skeins are dyed or sized if desired.

Sizing consists in passing the yarn through starch paste or other sizing materials, the primary object of the sizing being an increase in strength, so that the threads will not break under the tension to which they are subjected in the loom. The size also lays the loose fibers (*matte*) on the yarn. The size sometimes has substances added to it to increase the weight of the yarn.

Yarn in skeins is used for weft, when it is called *filling*, and it is wound off for the shuttle. The warp is *beamed;* that is, wound on iron spools or beams *a little longer* than the cloth is to be wide, with the threads untangled, arranged parallel, and colored threads in the places they are to have in the cloth. It is then ready for the loom.

Unsized yarn for warps, dyed or undyed, is sometimes wound off into section warps, an operation similar to beaming, except that part of the total number of threads is wound off on several beams. It is then sized, passing on to the beam.

After weaving, the final series of operations is *finishing;* the number of operations involved vary according to the kind and grade of material produced. In some cases, the loose fibers are burned off; in others, the material is *napped*, that is, a nap or felt is formed, as in flannelettes or cottonades. It may be sized with starch or other substances, stretched to its full width on the tentering machine, and ironed by passing between two hot rollers, *calenders*, which press upon each other with considerable force.

Count, *ply*, and *twist* refer to the yarn.

The *twist* varies with different kinds of yarn; the more it is twisted, that is, the harder the twist, the less easily is the yarn penetrated by the solutions used by the dyer. Warps always have a harder twist than filling (yarn for the weft), or hosiery yarn.

The *count* of a yarn indicates its fineness; the larger the count, the finer the yarn. With cotton yarn the count indicates the number of hanks of 840 yd. to a pound. Thus 60's cotton is a yarn that requires 60 hanks of 840 yd. to weigh a pound, or 60 × 840 yd. weigh a pound.

10 × 840 yd. of 10's cotton weigh a pound. The count of wool and linen is different from that of cotton.

The count of a cotton yarn may be found as follows: If y is the count, $y \times 840$ yd. weigh a pound, or 7000 gr., or $y \times 120$ yd. weigh 1000 gr. If we measure off 120 yd. and find its weight to be (a) grains, then the count of the yarn $y = \frac{1000}{a}$.

Or measure off 184 yd. and divide 100 by the weight in grams.

Ply indicates the number of strands composing a yarn. Two-ply yarn is composed of two strands twisted together, and so on. 3/30's cotton means that three strands of 30 count are twisted together, forming a compound yarn of 10 count.

The dyer may receive the material at any stage of its manufacture; as loose cotton, sliver or slubbing, yarn in the form of cops, skeins or warps, and as cloth.

CHAPTER VIII

LINEN — OTHER VEGETABLE FIBERS

Linen is the vegetable fiber next in importance to cotton. It is prepared from the stem of the flax plant, *Linium usitatissimum.* Very little linen fiber is produced in the United States. It is grown extensively in Northern Europe and Ireland.

The flax plant, besides the fiber, contains from 70 to 80 per cent of wood, pith, and other substances. The separation of the fiber requires a number of operations. The plant is pulled up by the roots, and drawn through coarse combs to remove seeds. It is next *retted*, a kind of fermentation which softens or destroys the substances which cement the fibers together and to the woody portion of the plant. After retting, various mechanical processes are employed to detach the ligneous matter from the fiber. *Breaking* consists in crushing the flax between grooved rolls, to break the woody particles; after which it is *scutched*, that is, the woody particles are beaten out by hand or by machines.

The last operation, *heckling*, consists in drawing the flax through coarse combs, then through finer and finer ones, until a degree of fineness suitable for spinning is attained.

Microscopic Appearance. — The linen fiber as spun consists of numbers of short cells, gummed together to form one long fiber. This is shown by a cross-section of the fiber (Fig. 2).

The individual fibers can be separated by treatment with dilute chromic acid. They appear as straight fibers, with a minute central canal. Their length is .8 to 1.5 in., diameter .0006 to .00148 in.

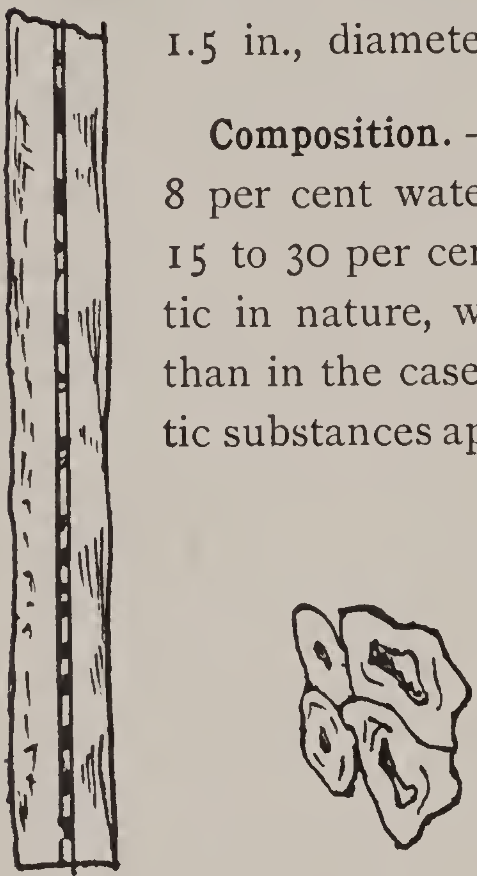

FIG. 2. — Linen fiber.

Composition. — Linen, unbleached, contains 6 to 8 per cent water, 62 to 77 per cent cellulose, and 15 to 30 per cent of other substances, mostly pectic in nature, which are more difficult to remove than in the case of cotton. The cellulose and pectic substances appear to be in chemical combination.

Properties. — Linen is stronger and more durable than cotton, less pliant and elastic, and possesses a peculiar luster. It is a better conductor of heat than cotton, which explains why linen articles are colder to the touch than cotton.

The cellulose of linen has the same composition and general properties as cotton cellulose. It is soluble in solutions of zinc chloride, ammoniacal copper oxide, and in concentrated sulphuric acid; forms nitrates and oxycellulose; is carbonized by acids; is oxidized by bleaching-powder, etc.

Linen is more easily tendered than cotton; the reagents act upon the substance which cements the individual cells together, separating them, and thus weakening the compound fiber.

Toward dyes and mordants, linen behaves like cotton, but it is more difficult to dye. The difference is probably due to the difference in the physical structure of the two fibers. We have seen that the structure of cotton influences its dyeing properties, in that unripe fibers, and solid places in the fiber, are dyed with difficulty. The presence of pectic substances on the fiber may also aid to render linen harder to dye than cotton. Dyeings on linen are usually required to have a high degree of fastness.

Detection of Cotton in Linen. — The presence of cotton in linen may be detected by microscopic examination. A number of other tests are also available, as for example: —

(*a*) The sample is placed in olive oil, removed and pressed between blotting paper. The linen becomes semi-transparent, while the cotton remains opaque.

(*b*) The sample is dipped in a 1 per cent alcoholic solution of fuchsine, washed, and laid in ammonia. Cotton remains uncolored, linen becomes rose-red.

Jute. — Jute is the fiber from the stem of several species of *Corchorus*, and comes most largely from India. It has been grown experimentally in the United States. Like flax, the plants contain much other material besides the fiber. The plants are steeped a week or more in stagnant water (retted); the bark is stripped, and the fiber rinsed, heckled, and dried. It is light yellow and has a high luster. Like linen, the filaments used (3 to 6 ft. long) are composed of bundles of small cells about an inch long.

Composition and Properties. — The jute fiber is fine and silky, but it cannot withstand dampness, and deteriorates rapidly under the best conditions. The bleached fiber also loses its whiteness, and in time oxidizes until it presents a yellowish brown color. Jute is used to a great extent for the manufacture of cotton bagging, matting, coarse cloth, and to some extent for curtains, carpets, and upholstery.

Jute differs from cotton and linen in that it contains no cellulose as such. It contains 9 to 12 per cent water, 86 to 89 per cent of a ligno-cellulose, and 2 per cent of ash, fat, and substances soluble in water.

The ligno-cellulose of jute is a compound of cellulose with lignified tissue, called *bastose*. Bastose is very susceptible to the action of acids and alkalies, and is easily destroyed by mineral acids. It absorbs chlorine with great avidity, and for this reason requires precautions when bleached with bleaching-powder.

Jute resembles cotton which has been mordanted with tannic acid, and it can be dyed directly with basic colors. It has also some affinity for certain acid colors.

Hemp. — Hemp is the fiber from the hemp plant, *Cannabis sativa*, largely cultivated in Russia and India, and to a considerable extent in the United States. The methods for obtaining the fiber from the plant are similar to those used for flax.

Hemp is principally used for the manufacture of ropes, canvas, and bagging. It is seldom bleached or dyed, as the fiber is too coarse. The fiber contains cellulose.

China Grass. — China grass or ramie is the fiber from the stem of a nettle, *Boehmeria nivea*, which is grown mainly in China, though it will grow well in this country. The fiber is difficult to detach from the woody matter; retting separates the fiber into its component cells, which cannot be separated from the stem and bark. The usual method of separation is to crush or beat the stalk while green, and wash out the broken wood, etc., by a powerful jet of water.

The fiber of China grass has a high luster and silky appearance, is little affected by moisture, easy to bleach, but difficult to dye without injuring its luster. It has a great variety of uses; curtains, laces, napkins, carpets, cordage, etc. The fiber is nearly pure cellulose.

Other Fibers. — Many other fibers have some commercial value, but most of them are seldom dyed or bleached.

Sun hemp is a bast fiber, used in India for cordage and sackcloth. *Manila hemp* is used for ropes and twine in this country, though it is said to be made into fine muslins in Manila. *Sisal hemp*, *New Zealand flax*, and the fibers obtained from the leaves of the aloe, agave, banana, palm, and the fibrous material which surrounds the cocoanut, have their uses.

Other Vegetable Materials. — *Straw* (for hats) is composed largely of cellulose, and is dyed and bleached. *Paper* is also more or less pure cellulose, and is often colored.

CHAPTER IX

ANIMAL FIBERS — WOOL

The animal fibers are totally different from the vegetable fibers in their composition and properties. Unlike vegetable fibers, they contain a large percentage of nitrogen; dissolve in warm solutions of alkalies; are not "carbonized" by acids; have a great affinity for dyes and mordants. The methods of preparing, bleaching, mordanting, and dyeing animal fibers are, as a rule, quite different from those used for vegetable fibers.

Wool. — Strictly speaking, wool is the hair of the sheep, but the hair of certain goats (cashmere, mohair, and alpaca) and of the camel are generally classed under the same category. *Fur* consists principally of the hair of the rabbit or hare and is extensively employed in the manufacture of the better class of felt hats.

Grades. — The grade of wool depends upon the length of the staple, its fineness, luster, strength, elasticity, color, curl, etc. It varies in different parts of the same fleece. Wool from diseased sheep is of inferior quality, being duller and having less affinity for dyestuffs than ordinary wool. Sheep pelts are often soaked in lime-water or sodium sulphide to loosen the wool, and the wool is pulled out before making leather of the skin. Such wool is known as pulled wool, and is of inferior quality.

Wool is divided into long-stapled and short-stapled varieties. These two varieties are usually separated before being spun. The long-stapled fibers are longer than 1½ in., are made up into *tops* and spun into *worsted* yarn; the shorter fibers (noils) are carded and spun into *woolen* yarn. In worsted yarn the fibers are more or less parallel; in woolen yarn they lie in all directions.

Microscopic Appearance. — When seen under the microscope (Fig. 3), the wool fiber appears in the form of a solid rod-shaped substance, the surface of which is covered with broad scales, all projecting in the same direction, like the scales of a fish. A more careful examination shows that a single fiber consists of a vast number of narrow individual cells, tapering toward each end. The interior cells appear to have a greater attraction for dyes than do the outer horny scales, and acids and some other additions to the dye-bath are supposed to aid in dyeing, in part by raising the scales, thus exposing the interior cells to the action of the dye.

FIG. 3. — Wool.

If a single wool fiber is taken between the thumb and finger of each hand and drawn gently, the end nearest the root remains stationary, while the other end slips. This is caused by the roughness or scales on the fiber. If, when wet, wool fabrics are subjected to friction, especially in presence of soap or of soap and soda, the friction of the fibers is greater in one direction than in the other, the scales interlock, and the material *felts*, becoming thicker, and assuming a denser appearance. *Milling* is used to produce this effect in the manufacture of broadcloths, flannels, and some other classes of goods. In some other classes of goods felting is a disadvantage, and must be prevented as far as possible.

The average length of the various classes of wool varies between 1½ and 7 inches, and the diameter from .004 to .0018 inch.

Kemps. — Kemps are smooth, white fibers, void of internal structure, and practically without "scales," since the scales are completely attached to the body of the fiber. They are frequently met with in the coarser varieties of wool, especially in mohair. A fiber may be normal up to a certain point, and thence kempy to the end, or even normal at both ends and kempy in the middle.

Having no scales, kemps have no felting power, and in dyeing they also come out uncolored or considerably lighter than the other fibers. Kemps are usually eliminated in the process of combing. Kemps have the same composition as ordinary wool. Their different behavior in dyeing is due to their impenetrable structure. They are analogous to the solid places found in cotton.

Dead fibers, so called, sometimes occur in wool. They are fibers which have been pulled out, or have died, before the wool was cut; they are harsh and weak, and are said not to dye readily.

Physical Properties. — Wool is hygroscopic, and takes up water from the air. At 100° C., wool becomes plastic and can be made to assume any shape desired, which it will retain if allowed to cool in this condition. Advantage is taken of this property, (*a*) in increasing the length of yarns; (*b*) in preventing the shrinkage of mixed goods containing wool when they are washed; and (*c*) in all the processes of wet finishing of woolen goods.

EXPERIMENT 49. — Place a horn spoon or spatula in a beaker of boiling water, remove it in 15 minutes, and bend it. When cool, its former shape cannot be restored unless it is heated again. Horn is similar in composition to wool, and the experiment illustrates the plasticity of wool.

Composition of Raw Wool. — Wool comes on the market in two conditions; *washed*, in which it was washed on the sheep before clipping, and *unwashed*.

Unwashed wool, or wool "in the grease," as it is called, contains water, fiber, and from 30 to 80 per cent of dirt and other substances which can be removed by washing, so-called *yolk* and *suint*.

As stated, the water content of wool varies according to the humidity of the atmosphere. In warm, dry weather it may contain 8 to 12 per cent, but in damp weather it may contain 30 per cent. Wool is sold on a basis of 18.25 per cent moisture. The quantity of moisture is determined at the time of the sale, an operation called "conditioning," which simply consists in determining the loss in weight of a sample dried at 105–110°.

Yolk consists of higher solid alcohols, especially cholesterol, free and in combination with fatty acids. It is insoluble in water, but forms an emulsion with soap solutions, and so can easily be removed by soap. Benzene and carbon bisulphide dissolve yolk.

Suint consists of the potassium salts of oleic, stearic, valeric, and acetic acids. It is soluble in water, and being a kind of natural soap, it removes the yolk, or a portion of it, when wool is washed with water.

The *dirt* is picked up by the wool and adheres to it mechanically.

The composition of raw wool varies considerably. It may contain:—

Yolk and suint	12 to 47 per cent.
Wool fiber	15 to 72 per cent.
Dirt	3 to 24 per cent.

Composition of the Fiber.—Chemically, the wool fiber differs from all others in its composition and properties. It consists of keratine, which is found also in all horny tissues, such as whalebone, horn, feathers, etc. The wool fiber varies in composition; thoroughly cleansed, it contains, on the average:—

Carbon	50 per cent.
Nitrogen	15 to 17 per cent.
Hydrogen	7 per cent.
Sulphur	2 to 4 per cent.

The presence of sulphur in wool distinguishes it from silk. Sulphur is detected in wool by boiling it with a solution of sodium plumbite, when lead sulphide is precipitated, causing the solution to turn black.

Sodium plumbite is prepared by treating lead acetate, or some other soluble lead salt, with sodium hydroxide:—

$$Pb(C_2H_3O_2)_2 + 4\,NaOH = 2\,NaC_2H_3O_2 + Na_2PbO_2 + 2\,H_2O.$$

EXPERIMENT 50. — Place about a gram of lead acetate in a test-tube with 5 or 6 cc. water. Add a dilute solution of sodium hydroxide until the precipitate, which first forms, redissolves. (Reaction.) Then add a piece of wool, and heat to boiling. What happens? The black precipitate is lead sulphide.

The presence of sulphur in wool sometimes gives rise to trouble in dyeing. If the water used contains lead (from pipes, etc.), the color of the wool is dulled by the formation of lead sulphide. The trouble can be avoided by the addition of sulphuric acid to the dye-bath, when lead sulphate is formed.

Solution of Wool. — Like cotton, wool cannot be dissolved without chemical change. *Concentrated mineral acids* dissolve wool completely. The action takes place slowly at the ordinary temperature, more rapidly on heating. When the solution is diluted and mixed with acid colors, insoluble compounds (lakes) are precipitated.

Nitric acid dissolves wool with copious evolution of fumes. The solution has a yellow color.

Solutions of *alkalies*, as caustic soda, or caustic potash, dissolve wool readily when the solution is heated. At the boiling temperature, one part of caustic soda will dissolve 100 parts of wool. The action decreases as the temperature sinks. At 0° C. wool is only slightly affected even by concentrated alkalies.

EXPERIMENT 51. — Dissolve 2 g. caustic soda in 100 cc. water, and add a piece of wool. Heat to a boil, and boil some minutes. What happens? Repeat, using cotton. How can you separate cotton and wool? Try the action of nitric acid on wool.

The solution of wool in alkalies contains a number of organic acids, the most important of these being *lanuginic* acid.

Lanuginic acid is a yellowish brown powder, soluble in water, and precipitated by many dyes, in the form of intensely colored lakes. It is precipitated by tannic acid, bichromate of potash, and the acetates of aluminium, iron, chromium, and copper, all of which are absorbed by the wool fiber. The existence of this substance with such properties is evidence in favor of the chemical theory of dyeing as applied to wool dyeing.

Chlorinated Wool. — Wool absorbs chlorine readily, and is destroyed by an excess of it. By careful treatment with bleaching-powder it may be made to absorb as much as 33 per cent of its weight of chlorine. Chlored wool resembles silk in some of its properties; it has an increased luster, but has become harsh and yellow, and lost its power of felting. It dissolves readily in ammonia with the evolution of nitrogen gas. It has also an increased affinity for certain coloring matters, and practical use is made of this property in preparing delaines for printing and for producing two-colored effects on woolen piece goods. In the latter case the wool is chlored before weaving, and dyed after weaving. The chlored wool takes up a greater quantity of the dye than the untreated wool.

Experiment 52. — Work two wool skeins 15 minutes in a 1 per cent solution of hydrochloric acid. Squeeze. Save the solution.

Grind 10 g. bleaching-powder to a paste with 20 cc. water, mix with 500 cc. water, and allow to settle. Take 100 cc., dilute to 300 cc., and work the two skeins in it 20 minutes. Work again in the first bath 10 minutes, squeeze, and wash 3 or 4 times. The product is chlored wool.

Dye a chlored and an unchlored skein together in a bath of 1 per cent diamine scarlet, 10 per cent Glauber's salt, and 1 per cent acetic acid in 500 cc. water, working carefully and boiling half an hour.

Dye a second chlored and unchlored skein in a bath of 2 per cent naphthol green B, 10 per cent Glauber's salt, and 2 per cent sulphuric acid in 500 cc. water. Test fastness to washing.

Diamine scarlet is a direct cotton color; naphthol green, an acid color. What effect has chloring on the affinity of wool for dyes?

Oxidation of Wool. — Wool is not readily oxidized; it may be boiled with bichromate of potash and sulphuric acid, in not too great quantities, without oxidation. If an excessive quantity is used, the wool is "overchromed"; when it has undergone this change, it can no longer be dyed black with logwood.

Boiled with permanganate of potash, the wool turns brown, and is tendered through oxidation.

Tendering of Wool. — Wool is tendered by a number of reagents. *Caustic alkalies* in warm or hot solution readily tender wool. *Sodium carbonate* does not tender wool at a moderate temperature, if the action is not too prolonged, but in boiling solution tenders wool readily.

Soap, *phosphate of soda*, *borax*, *ammonia*, and *ammonium carbonate* have little action upon wool, even in boiling solution, unless the soap is impure and contains sodium carbonate or caustic soda. Soap, phosphate of soda, and borax are often used when it is necessary to dye wool in an alkaline solution.

Absorptive Power. — Wool has an affinity for acids and absorbs them from dilute solutions. The acid absorbed cannot be readily extracted even by boiling water, and the wool can be dyed with acid dyes in neutral solution. (See Exp. 21.) Sulphuric acid, tartaric acid, and hydrochloric acid are taken up in this way.

Sulphurous acid is also absorbed and retained tenaciously by wool. Wool bleached with sulphurous acid, if it is to be printed, or woven with colored materials, must be treated with chloride of lime or hydrogen peroxide to destroy the excess of sulphurous acid. Otherwise the sulphurous acid may prevent the fixation of certain coloring matters, or cause them to fade, owing to its reducing action.

Tannic acid in cold solution has little effect on wool, but when boiled with it, the wool absorbs tannic acid, and its properties are altered.

Metallic salts, especially those of trivalent elements, such as aluminium, chromium, and iron, are decomposed by the wool fiber, and combine with it.

Behavior to Dyes. — We have seen that wool has a direct affinity for most dyestuffs, taking them up with such avidity, indeed, that in most cases its action must be tempered or moderated, so that the wool which first comes in contact with the dye will not get more than its share, and the goods be unevenly dyed.

We have seen that the direct cotton colors, the acid dyes, and the basic dyes can be fixed upon wool without the mediation of any mordant. The mordant colors, indeed, require a mordant, but it must be remembered that it is the compound of the mordant with the dye which produces the characteristic color, and that the dyestuff itself is, as a rule, valueless as a color.

Detection of Wool. — The simplest test for distinguishing between animal and vegetable fibers, is to pick out a few threads and burn them. The appearance and odor are characteristic.

Cotton, or any vegetable fiber, may be detected in wool or silk by boiling the material with a solution of caustic soda, when the wool dissolves completely, while the cotton is unaffected (see Exp. 49).

In *silk*, wool may be detected by boiling the solution with sodium plumbite; if wool is present, a black precipitate of lead sulphide is formed.

Carbonization. — Wool is separated from cotton for the purpose of remanufacture by the process of *carbonization*, which has already been mentioned under the head of Cotton. The material is saturated with sulphuric acid of 2° to 8° Tw., or hydrochloric acid, and dried. Drying chambers and continuous machines, such as are used in drying raw cotton, are used. After the operation, the cotton is beaten out.

Carbonized wool is less strong and lustrous than the fresh fiber, as the acid affects it to some extent. In dyeing it with acid dyes, caution is necessary.

Shoddy and Mungo. — Woolen rags from hosiery, flannels, and other soft woolen fabrics, are shredded for the purpose of remanufacture, and the product is called *shoddy*. *Mungo* is made from the shreds and clippings of milled woolen cloths. *Wool-extract* is prepared from mixed rags, which are carbonized to remove the vegetable fibers. These products, being made from colored rags, are more or less dark in color, and require precautions in dyeing.

Rare Wools. — *Cashmere* wool is the product of a goat which abounds in the mountains of Thibet. *Mohair* is the wool of the angora goat, imported from Turkey and South Africa. It is characterized by its striking luster. *Alpaca* is the hair of a goat. *Camel's hair* is a coarser hair, and is collected when the animals shed it. *Fur* consists principally of the hair of the rabbit and hare, and is extensively used in making the better class of felt hats.

Wool Manufacture. — Long wool fibers are combed and spun into worsted yarn, in which the fibers are parallel; the short fibers are carded, and spun into woolen yarn, in which the fibers are less regularly arranged. The loose wool passes through the intermediate stages of tops and slubbing before it becomes yarn. As the fibers are stiff, they are usually softened with oil before spinning.

Warps of wool are sized with gum or glue, to strengthen the yarn. For many kinds of cloth, the woven fabric passes through an operation known as *milling*. The cloth is wetted with soap and water, and is subjected to friction between two rollers until the material has felted to a sufficient extent.

Wool is dyed in the form of loose wool, tops, slubbing, skeins, warps, and cloth.

The *count* of worsted yarn is the number of hanks of 560 yards to the pound. The size of woolen yarns is indicated in Philadelphia and vicinity by the *cut;* the cut indicates the number of cuts of 300 yards to the pound.

Elsewhere, the *run* system is used, the run being 1600 yards. The run is divided into halves, quarters, and eighths. Two thousand yards of $1\frac{1}{4}$-run yarn weighs a pound. A pound of 6-cut woolen yarn contains 6 × 300 yards.

Fastness to Milling. — Dyes applied to wool before it reaches the cloth stage, as a rule, must be fast to milling, *i.e.* they must not run or bleed during that operation. Dyed cotton mixed with the wool must stand the same test.

The test is as follows: Plait together with yarn or mix with undyed material, knead for 20 minutes in a solution of 10 g. soap and 1 g. soda per liter of water, allow to lie 10 minutes, rinse, and dry.

CHAPTER X

SILK

Silk is the fibrous substance which the silkworm spins to form its cocoons. Silk resembles wool in many respects. The numerous kinds of silk may be divided into two classes — artificially reared and wild silk. The principal species of silkworm feeds on the leaves of the white mulberry, and is reared in China, Japan, India, Italy, the south of France, Greece, and to a slight extent in the United States. In Asia the worms are reared in the open air, but in Europe this is done in sheds. The eggs are placed on shelves, and the temperature of the room raised from 18° to 25° in twelve days. When the eggs hatch, the caterpillars are removed to another room, and fed on the leaves of the white mulberry. They grow rapidly, changing their skin every 4 to 6 days. At the end of 30 to 33 days the mature worms creep into birch twigs, or bundles of broom or heather, where they spin themselves into cocoons. The spinning lasts three days, generally, but in order to be more sure that all the worms have ceased spinning, five days are allowed to elapse before the cocoons are collected. Some of the finest having been selected for breeding, the rest are killed, either by exposing them in stoves to a temperature of 60–75° for three hours, or by steaming them for ten minutes.

How the Worm Spins. — Before the silk is spun, it is found in the worm as two liquids, one a clear, colorless liquid, the other colorless or yellow, which are both secreted from two glands, one on each side of the head, communicating with a capillary orifice in the head. The silk liquid solidifies on coming in contact with the air, forming a uniform double fiber, which in some places may be seen separated into two filaments.

Preparation of Silk. — After the cocoons have been sorted, the silk is *reeled* off. After removing the outer portion of the cocoon, which consists of a loose tangle of threads, a number of cocoons are placed in warm water, to soften the gum, and the ends of the fibers from 4 to 18 cocoons are collected and reeled off as one thread. The length of the fiber in a single cocoon varies from 1000 to 4000 yards.

Grades of Silk. — *Organzine* or warp silk is composed of the reeled off fibers of a number of cocoons. *Tram*, or weft silk, contains a smaller number of fibers. The outer portions of the cocoons are used in the manufacture of *floret* silk. Cocoons pierced, or otherwise defective, and the innermost layers of the cocoon are used for *spun* silk. They are fermented with water, boiled with soda, washed, dried, combed, carded, and spun.

The *count* of spun silk is the number of hanks of 840 yards to the pound. The size of raw silk is measured by the weight of 1000 yards in drams avoirdupois. A pound of 1-dram silk contains 250,000 yards.

Physical Properties. — Like wool, silk is hygroscopic, and absorbs moisture from the air. It can be made to absorb up to 30 per cent of water without feeling damp. The legal quantity of water in silk is 10 per cent, and it is sold on that basis, the moisture in each purchase being determined in "conditioning" establishments, as is the case with wool.

Silk is a bad conductor of electricity, and easily becomes electrified by friction. This is a disadvantage in manufacturing it, but it is overcome to a great extent by keeping the air of the room moist.

Silk is very strong; it is elastic, and can be stretched one-fifth to one-seventh of its length without breaking.

Under the microscope silk appears as a structureless, transparent, rod-like fiber with a smooth surface. It has an average diameter of .007 inches.

Composition. — Silk contains water, silk gum, and silk fiber, coloring matters, fats, and ash.

Water, as stated, varies with the dampness of the atmosphere.

Silk gum, or *silk glue*, is the outer covering of the fiber. It is soluble in boiling water, or a solution of soap, and makes up from 20 to 25 per cent of the raw silk. It consists mostly of *sericine*, $C_{15}H_{25}N_5O_8$, which is precipitated from solution by alcohol, tannin, and metallic salts.

Silk fiber, when purified from silk gum by treatment with hot water, and washed with alcohol and ether, has the formula $C_{15}H_{23}N_5O_6$, and is termed *fibroine*.

Ash. — The silk fiber contains a small quantity of inorganic mineral substances, from 0.7 to 1 per cent, forming the ash.

Raw silk also contains small quantities of waxy, fatty, and resinous matters, and in case of yellow silk, a yellow coloring matter.

Solution of Silk. — Silk can be dissolved in several reagents, at the same time undergoing a chemical change. *Concentrated mineral acids* dissolve silk readily and rapidly. Hydrochloric acid could be used to separate wool from silk, as the silk dissolves in a short time, while the wool requires several days.

Solutions of alkalies do not dissolve silk, or affect it appreciably when cold, even when concentrated, but hot solutions dissolve it readily, though not so readily as they do wool. *Sericinic acid* is a product of this action. It precipitates coloring matters from solution.

Experiment 53. — Boil a piece of silk with a 10 per cent solution of caustic soda. What happens?

Place a piece of silk and a piece of wool in concentrated hydrochloric acid. The silk dissolves almost immediately. Pour the solution into water. What happens? Let the wool and acid remain in contact until it dissolves. It will take several days.

Basic zinc chloride in boiling solution dissolves silk, but does not affect cotton or wool. Hence it can be used to separate silk from these fibers.

Experiment 54. — The basic zinc chloride is prepared by heating 100 g. zinc chloride and 4 g. zinc oxide, in 100 cc. water until solution is effected.

Try its effect on pieces of cotton, wool, and silk.

Nickel hydroxide dissolved in ammonia, dissolves silk very rapidly, and will not dissolve cotton or wool. It is used for the separation of silk from wool.

Experiment 55.—Dissolve 10 g. nickel sulphate in 1000 cc. water, and add a solution of caustic soda until the liquid is slightly alkaline. Allow the precipitated nickel hydroxide to settle. (Write reaction.)

Pour off the clear liquid, filter off the precipitate, and wash it with water. The precipitate is then put into a 100 cc. flask, 50 cc. ammonia (sp. gr. 0.90) added, and the volume made up to 100 cc. When the nickel hydroxide has dissolved, try its effect upon small pieces of silk, wool, and cotton.

Zinc chloride, in concentrated solution, and *copper hydroxide* dissolved in ammonia, dissolve silk and cotton.

Copper hydroxide in *caustic soda*, prepared by adding glycerol to a solution of copper sulphate, and then a solution of caustic soda until the precipitate which first formed just redissolves, is said to dissolve silk without affecting cotton.

Absorptive Power.—Like wool, silk has considerable affinity for many compounds.

Acids are absorbed from dilute solutions, and retained tenaciously. The luster of the silk is increased, and it acquires a peculiar feel, and emits a peculiar crackling sound when compressed. The *scroop feel*, as it is called, is frequently desired. Silk is usually *brightened* or given the scroop feel after dyeing, by working it in a dilute solution of acetic, sulphuric, or tartaric acid for a short time. Tartaric acid gives the best results. It is dried without washing. The effect of acetic acid disappears after a time, but that of the others is permanent.

Tannic acid is absorbed by silk, a property made use of in weighting silk (Chapter XII).

Metallic Salts.—Silk behaves like wool toward metallic salts used for mordants. It decomposes the salts even in cold solution.

Coloring Matters. — Silk behaves like wool toward coloring matters in general, but has less affinity for acid colors, and a greater affinity for basic colors.

Tendering of Silk. — Hot solutions of *caustic alkalies* tender silk. *Lime-water* destroys its luster, and renders it brittle. *Bleaching-powder* affects it, unless the solution is very dilute. *Sodium* or *potassium* carbonate affects it in warm solutions.

Oxidation of Silk. — Silk is much more easily oxidized than wool.

Potassium bichromate turns it yellow and injures it.

Potassium permanganate decomposes the fiber if applied in excess; in small quantity it turns it brown, and a subsequent treatment with sulphurous acid or bisulphite of soda bleaches the fiber.

Bleaching-powder, in very dilute solution, *chlores* silk, and increases its affinity for coloring matters, though not to the same extent as wool. In concentrated solutions it destroys the fiber.

Estimation of Silk, Wool, and Cotton. — Silk, cotton, and wool can be estimated accurately in fabrics, with the exception of plush, by the following method: —

A weighed portion is boiled for 10 minutes with a 1 per cent solution of hydrochloric acid, washed well, dried at 100° C., and weighed. The acid removes dye and size. The weight is the weight of cotton, silk, and wool.

The silk is dissolved by treating for two minutes with a cold solution of nickel hydroxide in ammonia (see Exp. 55), the residue digested for two or three minutes in a boiling solution of hydrochloric acid (1 per cent), washed, dried at 100° C., and weighed. The residue is the cotton and wool.

The residue is boiled with a 2 per cent solution of soda, washed, dried at 100° C., and weighed. The residue is cotton.

Wild Silks. — *Eria* silk is found in India; *muga* silk is a native of Assam in Africa; *yamomi* silk comes from Japan; all these come from caterpillars. *Sea silk*, or *byssus*, is composed of fibers excreted by certain mollusks for the purpose of attaching themselves to rocks, and comes from Sardinia and Corsica in the Mediterranean Sea.

Tussur silk is the most important of the so-called wild silks. It comes from India and China, and is used principally for the manufacture of artificial sealskins. Tussur silk is the product of a caterpillar.

Under the microscope, tussur silk appears as a flat, double fiber, each of which individual fibers can be split up into six to eight little fibers or fibrillæ by suitable treatment.

Composition and Properties of Tussur Silk. — Raw tussur contains about 5 per cent ash, and about 25 per cent *silk gum.* Its *fibröine* (fiber constituent) contains less nitrogen and more oxygen than ordinary silk.

Tussur silk is much stiffer than ordinary silk, and has a brown color which is difficult to remove. It is more difficult to dye than ordinary silk.

Caustic soda in solution dissolves tussur silk much less readily than ordinary silk; *concentrated hydrochloric acid* and *chromic acid* act in the same way.

Detection of Tussur Silk. — This may be effected as follows: —

(*a*) By microscopic examination of the fiber.

(*b*) By boiling with a 10 per cent solution of caustic soda, which dissolves ordinary silk or wool in about 10 minutes.

(*c*) By concentrated hydrochloric acid, which dissolves ordinary silk instantly, tussur silk only slightly even in 24 hours.

CHAPTER XI

OPERATIONS PRELIMINARY TO DYEING — BLEACHING COTTON AND LINEN

As they come into the hands of the dyer, the textile fibers are in a more or less impure condition, and as a rule, must go through preparatory processes before they are ready for the actual dyeing operations. Besides the natural impurities, yarns gather dirt and oil from the machinery, and cloth, in addition, contains the ingredients of the size used to strengthen the warp in weaving.

Cotton contains natural fats and waxes. Woolen yarn or cloth usually contains considerable quantities of oil added to facilitate the weaving, and silk contains a gum which must usually be removed before dyeing. All textile fibers contain natural coloring matters to a greater or less extent. Cotton warps are sized with tallow, starch, gums, China clay, paraffin wax, and other substances. Wool warps are sized with glue, for the most part.

Objects. — The objects of the preliminary operations are as follows: —

(1) To wet the material so that every portion of it will be uniformly penetrated by the solution of mordant or dye, and not be protected from actual contact with it by bubbles of air, etc.

(2) To remove impurities, such as oil or grease, which

would prevent the mordant or dye from being taken up by the fiber.

(3) To remove natural coloring matters when they would interfere with the brilliancy of the color to be produced.

In this chapter we will only deal with the processes for preparing cotton and linen for dyeing.

COTTON

Wetting Out. — When dark shades are to be dyed, or light colors of no particular brilliancy, the only preliminary operation necessary is wetting out. This only aims at wetting the material evenly, and is accomplished by boiling the goods with water, or with water containing a little sodium carbonate (soda ash). Sodium carbonate aids in removing the natural fats, and also removes any oil stains that may be present. Very often, however, it is omitted, and its omission is a necessity when dyes are to be used whose colors are affected by sodium carbonate, as it is difficult to wash the material free from traces of this salt.

Raw cotton is often not wetted out before dyeing. It is usually wetted out in the machine used for dyeing it by placing it in the machine and boiling with water until it is thoroughly wet.

Warps and skeins are sometimes wetted out in the dyeing machines, but usually in kiers. A kier (Fig. 4) consists of a cylindrical wooden or iron vessel (*A*) provided with a top (*B*), which can be fastened down tightly. Large stones are placed in the bottom of the kier, or there is a perforated false bottom. The yarn is packed in around a central iron pipe, the puffer pipe (*C*), which terminates in a hood (*D*), and is so arranged that when a jet of steam is sent in at the bottom it forces the water up the pipe and showers it over the goods. The liquid then finds its way to the bottom of the kier, ready to be forced up again. The circulation of the liquid insures thorough treatment of every part of the goods.

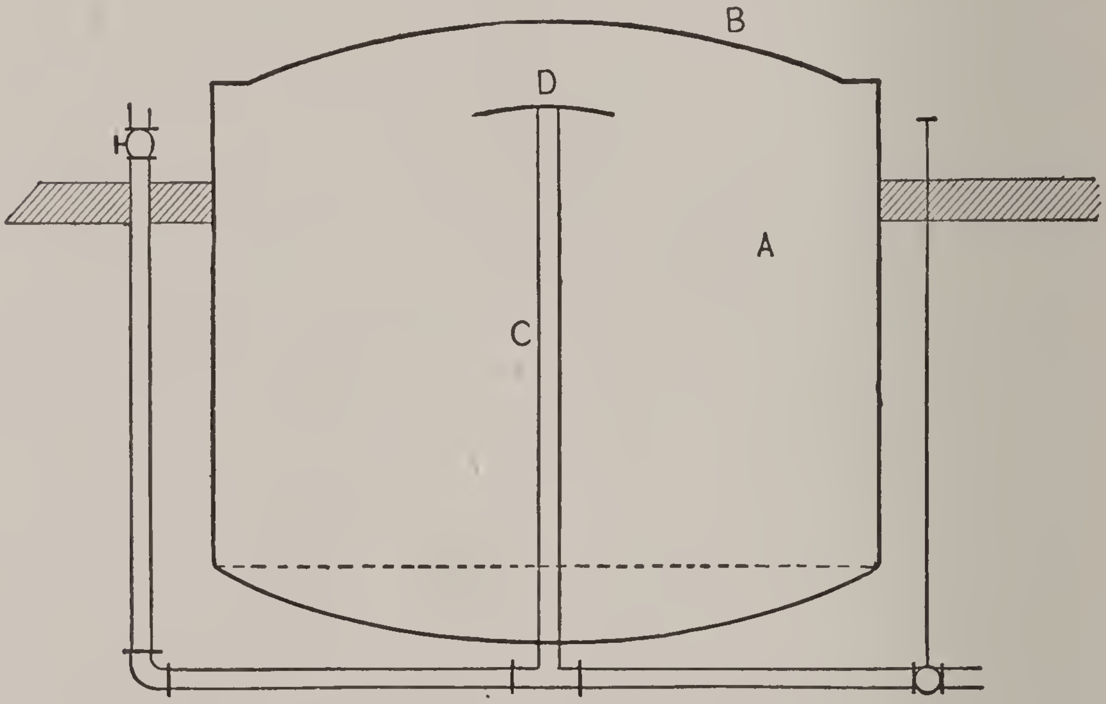

FIG. 4.—Low-pressure kier.

Wooden kiers are arranged to work at the ordinary atmospheric pressure, or a little above. Iron kiers may be for low pressure (that is, from 5 to 15 pounds), or high pressure (working under a pressure of 40 to 50 pounds).

The construction of the kier varies somewhat according to the pressure at which it is to work.

Bleaching.—The objects of bleaching are as follows:—

(1) To remove the natural brown coloring matters, which have a dulling effect upon bright and brilliant colors, and

whose removal is a necessity for the production of beautiful shades.

(2) To prepare pure white goods for the market (market bleach).

The methods used in bleaching vary extremely, according to the material to be bleached, and the effects desired. Dark, low-grade cotton naturally requires more vigorous treatment or a greater number of operations than high-grade cotton. Fine yarns and delicate fabrics must be handled more tenderly than coarse materials. Some kinds of dyeing require an extremely fine bleach, while a very simple bleach suffices for others.

The number and exact nature of the different bleaching operations vary in different mills for the same materials; they also depend somewhat on whether a half bleach, a three-quarter, or a full bleach is desired.

Chemistry of Bleaching. — There are two stages in every process of bleaching. The first consists in a treatment with alkalies for the removal of natural or acquired fats and oils, size, etc., and may be called *saponification*. The second consists in the removal of coloring matters, and is called *decolorization*.

Saponification. — Animal or vegetable fats are compounds of certain organic acids, mainly palmitic, stearic, and oleic acids, with glycerol, being in the nature of salts. When boiled with sodium carbonate, caustic soda, or lime, the fat is decomposed, glycerol and a salt of the fatty acid being formed.

$$\underset{\text{Fat (palmitin).}}{C_3H_5(C_{16}H_{31}O_2)_3} + 3NaOH = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Sodium palmitate.}}{3NaC_{16}H_{31}O_2}.$$

The sodium or potassium salts of these acids is ordinary soap, and the process of making them is called *saponification.* Cotton wax, mineral lubricating oils, and paraffin wax are not saponified or made soluble in water by alkalies. A soap solution, however, has the power of removing these substances in the form of minute drops suspended in the liquid, that is, as an emulsion. But if present in too large quantity, mineral lubricating oil or paraffin wax are not removed, and the result is a stain in the finished goods.

Methods. — There are two general methods of saponification: —

(1) The saponification is accomplished directly by boiling the cotton with solutions of caustic soda, or sodium carbonate, sometimes with addition of resin.

(2) This method is applied to cloth only. The saponification is accomplished in several stages: —

(*a*) Boiling with lime-water under pressure, an insoluble lime soap being formed.

(*b*) The lime soap is decomposed by an acid: —

$$CaAc_2 + 2\,HCl = CaCl_2 + 2\,HAc.$$

(*c*) Boiling with resin soap under pressure, and

(*a*) Boiling with soda ash under pressure.

These last two operations remove the fatty acids, dissolving them in the form of their sodium salts. The resin soap probably aids in emulsifying mineral oil and waxes.

Decolorization. — After grease, waxes, etc., have been removed by saponification, the cotton still retains a light brown color. The second stage in bleaching consists in the oxidation of the color. The success of this operation depends upon the thoroughness with which the preceding operations of saponification have been carried out. The color may be partly or completely removed, according as a partial bleach or a full bleach is desired.

The oxidizing agents used in bleaching are: —

(1) Chloride of lime, or bleaching-powder, and sodium hypochlorite.
(2) Potassium permanganate.
(3) Hydrogen peroxide.

Decolorizing Agents. — Bleaching-powder ($Ca(OCl)_2$) is a white powder with the odor of hypochlorous acid. It is soluble in twenty times its weight of water, but always leaves some undissolved residue. When treated with an acid, as sulphuric or hydrochloric acid, it gives up all its chlorine. Thus, with hydrochloric acid the reaction is as follows: —

$$Ca(OCl)_2 + 2\,HCl = CaCl_2 + 2\,HClO,$$

$$2\,HCl + 2\,HClO = 2\,H_2O + 2\,Cl_2.$$

EXPERIMENT 56. — Add hydrochloric acid to a little bleaching-powder in a test-tube. What is given off? Write reaction.

Color 500 cc. water *faintly* with a little aniline blue, and add bleaching-powder solution. What happens? Repeat, using fuchsine; using methylene blue.

In bleaching, bleaching-powder is aided to a great extent by the carbonic acid of the air, which liberates hypochlorous acid, and the latter acts readily upon the color to oxidize it: —

$$Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2\,HClO,$$

$$HClO = HCl + O.$$

The hydrochloric acid acts upon the chloride of lime, liberating more hypochlorous acid.

After the goods have been treated with bleaching-powder, they are washed and treated with dilute acid, to complete the decomposition of the bleaching-powder, and to dissolve calcium carbonate. Sulphuric acid, hydrochloric acid, or acetic acid may be used. When mineral acids are used, the fiber must be washed very carefully to prevent tendering, a precaution not necessary for acetic acid.

Antichlorine compounds, consisting usually of a solution of sodium acid sulphite ($NaHSO_3$), are often used to remove all traces of chlorine from the fabric.

EXPERIMENT 57. — Bleach two skeins of cotton yarn, regular yarn, and a low-grade, dark yarn as follows: —

(1) Saponification. Boil for half an hour in 500 or 600 cc. water with 4 per cent sodium carbonate. While boiling, prepare the bleaching-powder solution for (2). What is the color of the solution of sodium carbonate after the yarn has been boiled in it? Is the yarn darker or lighter than before?

(2) Decolorization. Grind 5 g. bleaching-powder with 20 cc. water in a mortar, pour into 500 cc. water, and wash the contents of the mortar into it. Stir well, and allow to settle; the liquid will not become perfectly clear.

Pour the liquid over the skeins, work for 5 minutes, and allow to stand half an hour. Without washing, enter the yarn in a bath of 3 cc. concentrated hydrochloric acid in 500 cc. water. Enter the yarn, and work 5 minutes. Wash well and dry. What is the difference in color between the two skeins?

Sodium hypochlorite ($NaClO$) is sometimes used for bleaching in place of bleaching-powder. It is prepared by treating a solution of bleaching-powder with the proper quantity of sodium carbonate: —

$$Ca(OCl)_2 + Na_2CO_3 = CaCO_3 + 2\ NaClO.$$

The precipitated calcium carbonate is allowed to settle, and the clear solution drawn off. Its properties are similar to those of bleaching-powder.

Sodium hypochlorite is the active agent in electrolytic bleaching processes. It is prepared by passing an electric current through a solution of common salt, under suitable conditions.

Hydrogen peroxide (H_2O_2) is too expensive for use in cotton bleaching, except in rare cases. It is applied to cotton by a method similar to that used for wool (Chapter XII).

Potassium Permanganate. — This salt is sometimes used in cotton bleaching in neutral or acid solution. The reaction in acid solution is as follows: —

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

In neutral solution, manganese dioxide is precipitated on the material.

$$2\,KMnO_4 + H_2O = 2\,KOH + 2\,MnO_2 + 3\,O.$$

The manganese dioxide, which imparts a brown color to the goods, is removed by treatment with sulphites.

$$MnO_2 + H_2SO_3 = MnSO_4 + H_2O.$$

Oxycellulose. — During the process of bleaching by bleaching-powder or potassium permanganate, the cellulose probably undergoes a slight oxidation to oxycellulose, but under proper conditions no injurious action takes place. Under certain conditions oxidation may go too far, with the result that the fiber is weakened, or tendered. This action has already been referred to (see Tendering of Cellulose).

Bleaching Loose Cotton. — Loose cotton is sometimes bleached. The operations may be conducted in the apparatus for dyeing loose cotton (Chapter XIII), or in wooden vats provided with a false bottom, the cotton being stirred with poles.

The methods vary; the following is an example: —

(1) *Ley Boil.* — The cotton is boiled with sufficient water, and 2 to 3 per cent of its weight of sodium carbonate.

(2) *Chemicking.* — The cotton is saturated with a clear solution of bleaching-powder at ½ to 2° Tw.; after an hour or more the liquid is drawn off, and the moist cotton allowed to remain undisturbed for some hours. It is then washed.

(3) *Souring.* — The cotton is treated with acid at ½ to 1° Tw. washed, hydro-extracted, and dried.

Yarn Bleaching. — Yarn is bleached as warps or skeins, more rarely on the cop; cop bleaching requires special apparatus.

The series of operations is as follows: (1) ley boil, and wash; (2) chemic, and wash; (3) sour, and wash.

Ley Boil. — The yarn is boiled for 6 to 10 hours with 3 to 6 per cent sodium carbonate (soda ash), or with caustic soda, or a mixture of the two. Caustic soda saponifies the cotton oil more readily than sodium carbonate. The boiling is conducted in a high or low pressure kier, and the duration of the boil depends on the pressure in the kier. With a high-pressure kier, the operation requires less time.

Skeins are linked into chains 6 feet long or longer, or they may be left separate if a skein-washing machine is at hand. Warps, if long, are doubled two, three, or four times to reduce their length, or are linked up in slip-knot formation, — their ends are tied together to prevent entanglement. The yarn is packed evenly in the kier, so that the solution will circulate through it, and not through channels between the bundles of yarn. It is covered with coarse linen cloth, and weighted down with beams. Sufficient water must be used to cover the goods completely and insure that they do not come in contact with the air during the operation, which would tender them by oxidation. Iron kiers should be kept covered with lime, as the bare iron will produce stains on the yarn. Hard water sometimes produces stains, due to the formation of a brown insoluble calcium salt of cotton oil, which is difficult to remove in bleaching.

After boiling, the yarn is washed partly in the kier, and the washing is completed in washing machines, described later. It is then hydro-extracted, and chemicked.

A second ley boil is often given.

Chemicking. — The success of this operation depends on the thoroughness of the ley boil. The yarn is treated with a solution of bleaching-powder of ½ to 1° Tw., according to its fineness. Some bleachers allow it to remain in this liquid 3 or 4 hours, and then remove and sour, while others draw off the solution and allow the yarn to lie exposed to the air for some time before souring. For very fine yarns, which are easily tendered by a bleach liquor which is too strong, the strength of the liquid should be determined by titration. The method is given later.

The chemicking, souring, and washing may be conducted (Fig. 5) in a stone or wooden cistern (*A*), provided with a false bottom (*B*), into which the yarn is laid or packed evenly so as to secure an even circulation. The liquid with which the yarn is to be treated is raised by means of a pump (*C*) from a well below the floor into a perforated wooden tray (*D*), which showers it over the goods. It percolates through the goods, accumulates below the false bottom, and flows back into the cistern. A circulation of liquid is thus kept up during the entire operation. The strength of the liquors must be restored from time to time. This apparatus is called the *sieve*, and the operations *chemicking under sieve*, etc. The chemic and acid act upon the pump, necessitating frequent repairs.

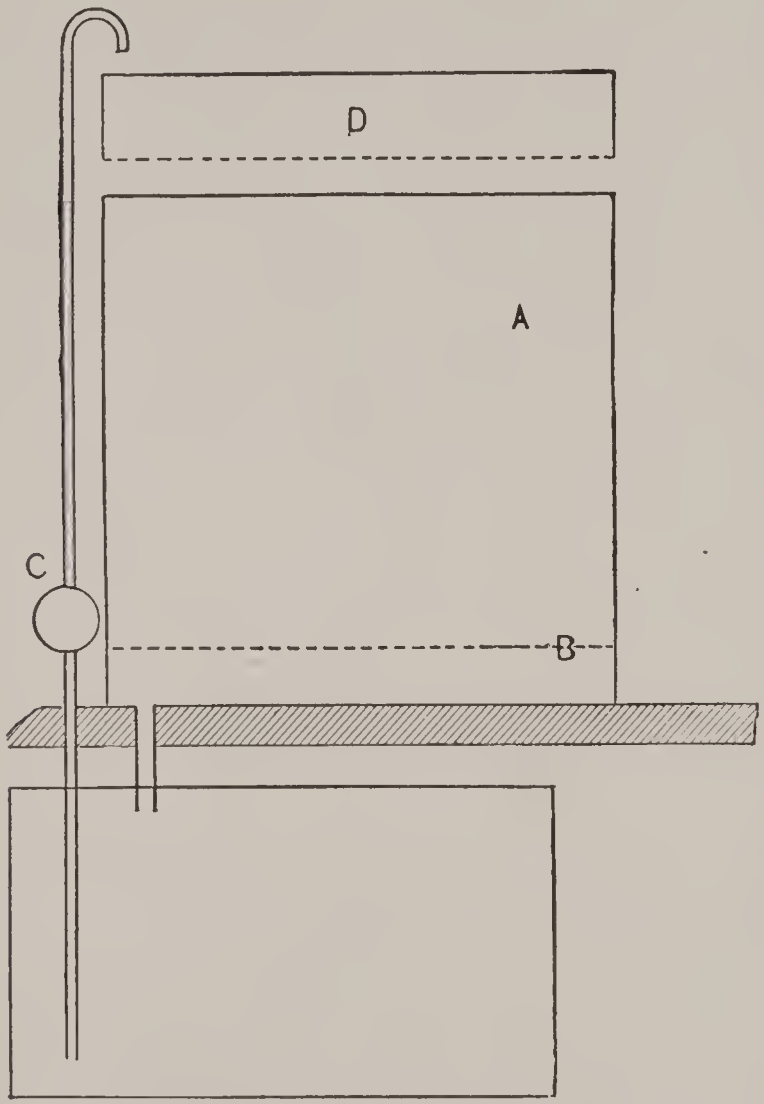

FIG. 5.—Bleaching under sieve.

The chemicking may also take place in plain wooden vats or cisterns, the yarn being thrown into the liquid. At the end of the operation, the bleach liquor is, as a rule, only half exhausted, and is pumped off into an empty cistern, and used again after its strength has been restored.

Souring.—Sulphuric, hydrochloric, or acetic acid of from 1 to 2° Tw. are used. The yarn is then carefully washed.

Cop Bleaching. — In cop bleaching, the hot alkaline liquor and the cold bleaching liquors are forced through the cop by apparatus described under cop dyeing. Sodium hypochlorite is usually used in place of calcium hypochlorite.

Preparing the Chemic. — To prepare the bleaching liquid, a sufficient quantity of chloride of lime is thoroughly mixed with water — at least three gallons of water per pound of bleaching-powder — in wooden or stone vessels, and the solution allowed to settle. For 1000 pounds yarn, about 30 pounds bleaching-powder are required. The clear solution is drawn off and diluted to the desired strength.

For dissolving the chloride of lime a special apparatus is in use. It consists of a square cast-iron, lead-lined vessel, containing a wrought-iron perforated drum, also lined with lead. After the bleaching-powder has been placed in the drum with sufficient water, it is revolved until solution is complete. The solution is drawn off by means of a tap, placed at a sufficient distance from the bottom to avoid disturbing the sediment.

Control of the Chemic. — The chemic, sour, and many other solutions of the dyer are made up approximately to some desired strength by the aid of hydrometers, since the density of a solution varies with its strength.

The hydrometer is an instrument to measure the density of a liquid, by being placed in it. It is constructed on the principle that a floating body will sink in a liquid until it has displaced its own weight of the liquid. The instrument consists of a glass bulb connected with a graduated stem. Below the bulb is a smaller bulb of mercury to hold the instrument upright. The instrument is placed in the liquid to be tested, and the reading at the point to which it sinks gives the density of the liquid.

Hydrometers are graduated in several ways, the most important being as follows: —

(1) *Specific Gravity Hydrometers.* — The scale on the stem of this instrument shows the specific gravity of the liquid.

(2) *Twaddle Hydrometer.* — The scale is so divided that degrees Twaddle can be converted into specific gravity by multiplying by 5, adding 1000, and dividing by 1000.

For example, 10° Tw. = 1.050 specific gravity.

(3) *Baumé Hydrometer.* — This is often used. There is no simple relation between degrees Bé. and specific gravity. A table can be used for converting them.

The indications of a hydrometer are sometimes not delicate enough, and in other cases its indications are misleading. In such cases recourse must be had to chemical methods.

Titration of the Chemic. — The strength of a solution of bleaching-powder is reduced when it is used, without a corresponding reduction in its density. To ascertain the strength of bleach liquors which have been used, so that they can be restored to the proper strength, a portion must be withdrawn and titrated according to the following method: —

4.95 g. of finely powdered arsenious oxide are dissolved in 15 cc. glycerol with the aid of a gentle heat, and the solution diluted to a liter. 25 cc. of the solution are placed in a beaker, diluted to 100 cc. with water, and 1 cc. of a solution of indigo carmine added. Before bleaching, a sample of the bleach liquor is run slowly into this solution from a burette until its color is just discharged. After bleaching, the operation is repeated.

The volume of the bleaching liquid required to effect the decolorization varies with its strength. If 20 cc. are required before bleaching, and 40 cc. afterward, the strength of the liquid has decreased to $\frac{20}{40}$ or $\frac{1}{2}$ of its former power, and its strength can be restored by adding one-half the quantity of the strong solution of chloride of lime used in preparing the bleaching liquid at first. If 20 cc. are required before, and 60 cc. afterward, to decolorize the solution of indigo carmine and arsenious acid, the bleach liquor is only $\frac{20}{60}$ or $\frac{1}{3}$ as strong as it was at first.

The indigo carmine solution is prepared by dissolving 1 g. indigo carmine in 500 cc. water.

When fine yarns or delicate fabrics are to be bleached, the strength of the bleach liquor is best determined by a chemical method instead of by the hydrometer, since too strong a solution may cause tendering. The method just described may be used to test the strength of the solution.

Control of the Sour. — After once using, the density of the sour is no indication as to its strength. Its strength must be determined by titration, as is the case with the bleach liquor, and it can then be restored to the required degree of activity by the addition of fresh quantities of acid. The method for dye-house work is as follows: —

Dissolve 4 g. of chemically pure caustic soda in 1000 cc. water. Dilute 20 cc. of the sour to 100 cc., add a few drops of a dilute solution of methyl orange, and add the caustic-soda solution slowly from a burette until the color of the solution just changes. After using, the liquid can be titrated again and made up to its original strength by the addition of acid. The solution of caustic soda should be protected from the air.

Cloth Bleaching. — Three essentially different processes of bleaching cloth are in use, namely, the market or white bleach, the Turkey-red bleach, and the printer's bleach.

The object of the *market bleach* is to produce a white which will please the eye of the customer.

The *Turkey-red bleach* prepares the goods for dyeing or printing with alizarine, or the production of Turkey-red.

The *printer's bleach* is preliminary to calico printing. It is the most perfect of the three, as every impurity which would attract dye must be removed.

Printer's Bleach. — The general outline of the printer's bleach is as follows: the cloth passes through most of the operations in the form of a rope, the different pieces being sewed together, end to end.

(1) *Singeing.* — The loose fibers are burned off by passing the cloth over a row of Bunsen burner flames, or over a heated metal plate or roller.

(2) *Singeing Wash.* — The cloth is washed to remove as much of the loose charred fibers as possible. In the washing machine (Fig. 6) the cloth passes between squeezing rollers (*A*), then under another roller in a trough of water (*B*), again through the squeeze rollers (*A*), and through the water, and so on a number of times until it passes away at the end. Clean water constantly flows into the trough.

(3) *Lime Boil.* — The cloth is limed with milk of lime, in a machine similar to the washing machine though constructed somewhat differently, run into an iron kier, cov-

ered with water, and boiled under 15 to 50 pounds' pressure for 6 to 10 hours. From 5 to 7 pounds of lime are used per 100 pounds of goods. When the lime-water is run off, the kier is filled as rapidly as possible with cold water

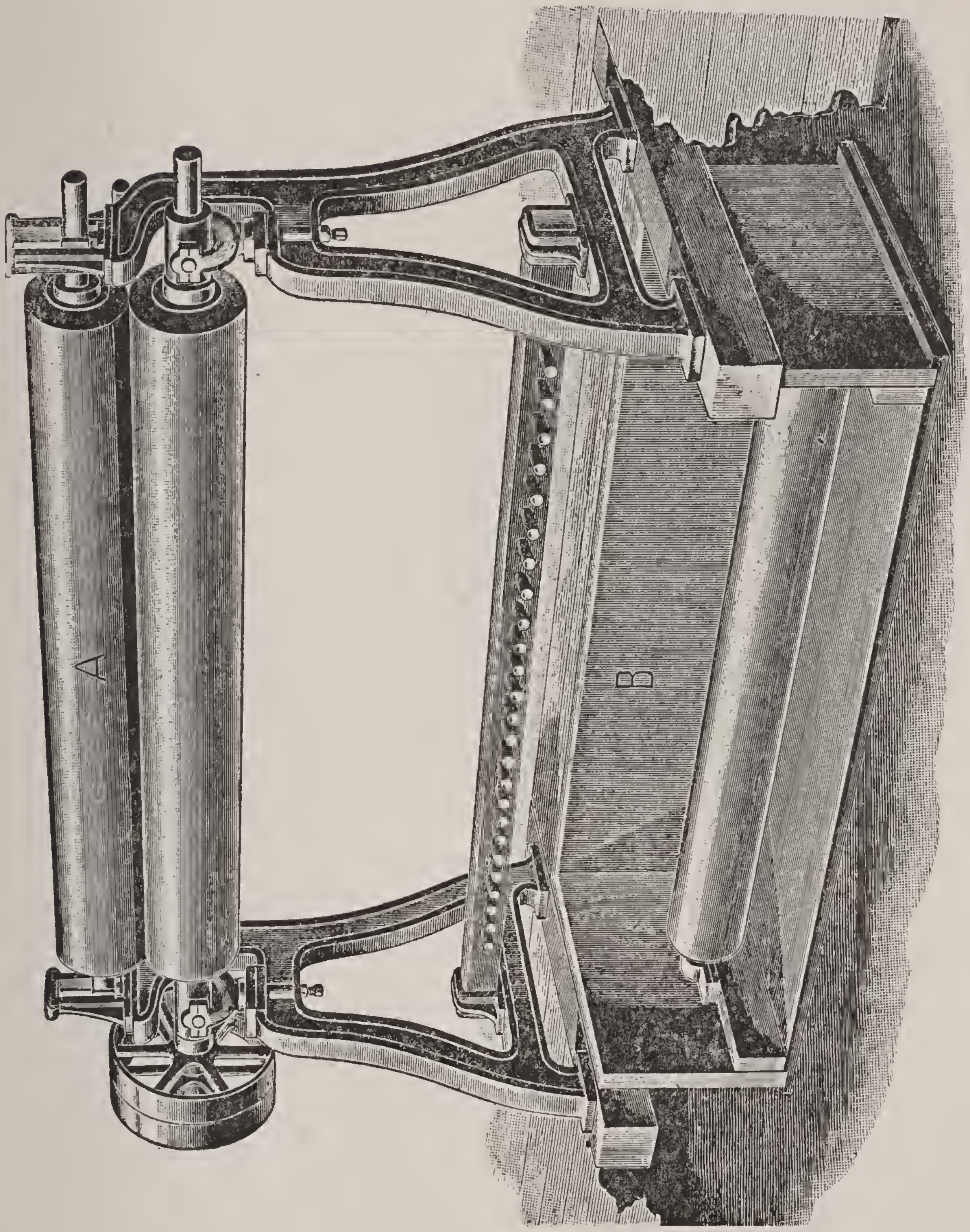

FIG. 6.—Cloth washing machine.

to prevent the lime from drying where it is in contact with the hot sides of the kier, which will cause tendering or brown stripes on the goods.

(4) *Lime or Gray Sour.* — The cloth passes through hydrochloric acid of 2° Tw. in a machine similar to the washing machine, the sour being kept to a uniform strength by titration of the solution and additions of acid from time to time. The cloth is then washed in a washing machine.

(5) *Ley Boil.* — The cloth is boiled in kiers with a solution of soda ash (1.7 to 3.0 per cent of the weight of the cotton), or caustic soda (1.2 to 1.5 per cent), for 3 to 5 hours in a high-pressure kier, and washed.

(6) *Resin Boil.* — The cloth is boiled with resin soap and caustic soda for 7 to 12 hours. Resin soap is prepared by boiling resin in a solution of sodium carbonate of about 20° Tw. until it dissolves. Resin floats on a solution of this strength, and dissolves more quickly than in a more dilute solution.

(7) *Chemicking.* — The cloth passes through a solution of bleaching-powder of ½ to 1° Tw., in a machine similar to the washing machine, is piled up in a heap, and allowed to lie over night. It is generally washed before souring.

(8) *White Sour.* — The goods are passed through hydrochloric, sulphuric, or acetic acid at 1° to 2° Tw.

(9) *Final Washing.* — The machine already described may be used. A more effective machine is the square beater washing machine (Fig. 7). The pieces, stitched together, pass in the form of a rope between two squeeze rollers (*A*), then under a square beater (*B*), directly beneath in the water, along under the surface of the water to another roller (*C*), and back to the squeeze rollers (*A*).

The pieces follow the same course over and over again in a spiral direction, until they leave the machine. In passing the square beating roller, which revolves in a direction opposite to that followed by the pieces, the cloth opens out from the rope form to almost its full width, and at the same time receives a flapping motion as it passes along the surface of the water.

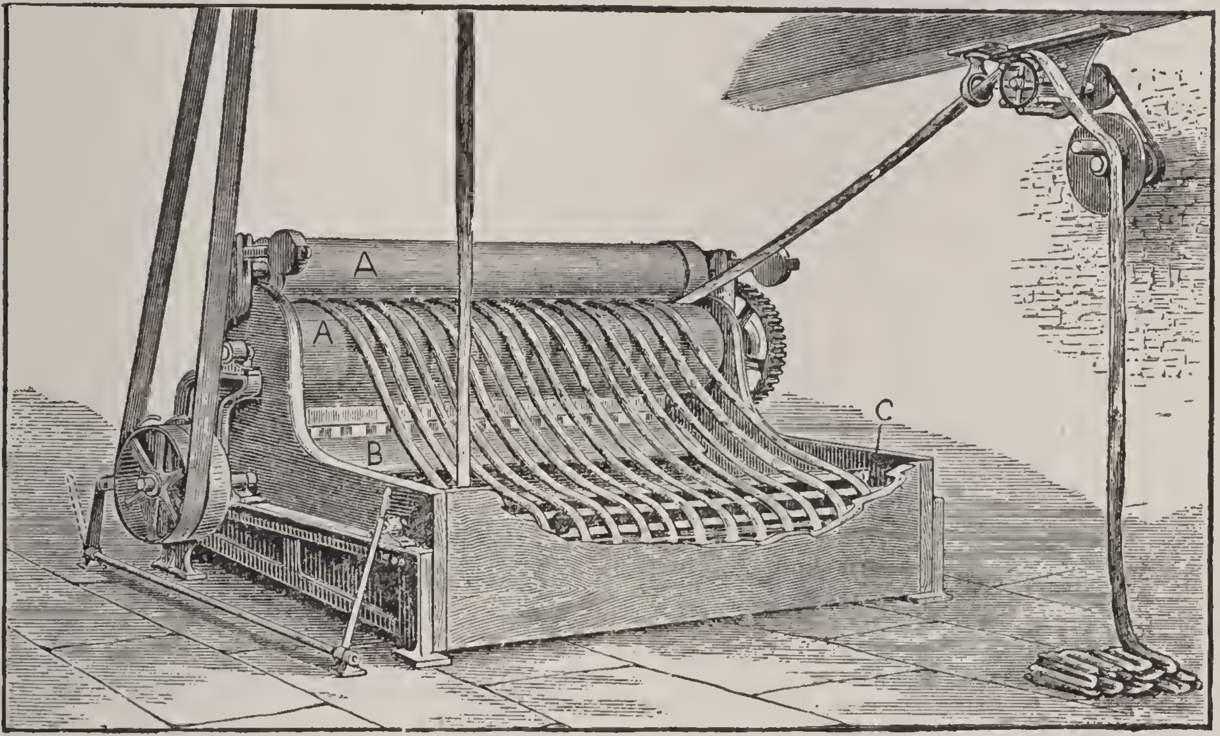

FIG. 7.—Square beater washing machine (Mather and Platt).

Market Bleach.—The methods and machinery adopted for the market bleach depend to a great extent on the nature of the goods. Ordinary cloth is made into the rope form, and the same machines may be used as in the printer's bleach. Light fabrics are dealt with in the form of bundles or lumps, and the chemicking and souring are done in cisterns as in yarn bleaching.

For washing light fabrics, the *dash wheel* may be used. The goods are put in the compartments of a drum, which is caused to revolve, and at the same time a current of water flows in and washes the goods. The speed of the drum should be such that the goods are thrown from side to side of the compartments. A similar machine is used in leather dyeing.

For the market bleach, singeing is generally omitted, soda ash is substituted for resin soap in the resin boil, and many dyers omit the lime boil. After bleaching, the goods are *blued*, *i.e.* passed through water containing a small quantity of a blue coloring matter, which neutralizes a slight yellow tinge of the goods.

Turkey-red Bleach. — For goods to be dyed Turkey-red, bleaching with chloride of lime is generally omitted. The goods are boiled with water, given one or two ley boils, soured with sulphuric acid, washed, and dried.

Defects in Bleached Goods. — Defects may be due to iron stains, oil stains, and oxidation of the fiber.

Iron stains appear as red spots, and are apt to be produced when rusty machinery comes in contact with the goods, or when the iron kier is not completely coated with lime. They may also be produced by the use of water containing too much iron, and by the dropping on the cotton of lubricating oil charged with iron derived from the wear of the machinery. Iron stains are hard to remove. They may often be removed by saturating the spot with strong hydrochloric acid, and washing.

Oil stains occur as bright yellow stains in various shapes, and often do not appear until some time after the goods have been sent out. They may be due to the use of paraffin wax in sizing the warps, or to the use of mineral oils for lubricating, since lubricating oil very often gets on the goods. The paraffin wax or mineral oil cannot be saponified, and can only be removed when properly mixed with tallow or other fat, or with animal or vegetable oil, as the case may be. If the paraffin is not removed, when the goods are chemicked the paraffin takes up chlorine, forming compounds which turn yellow when exposed to light and air. Such oil stains may be removed by saturating the spots with a little olive oil, and boiling in weak caustic soda after the oil has soaked in thoroughly.

Injury through oxidation of the fiber, appearing as tendering in spots or stripes, may be caused: —

During the *lcy boil*, by the goods coming in contact with the air.

During the *lime boil*, by the fabric coming in contact with the air, or by lime being dried upon it by the hot sides of the kier.

During the *bleaching*, by the use of too strong solutions of bleaching-powder, or by particles of undissolved bleaching-powder coming in contact with the material.

Injury by over-oxidation may be detected by means of methylene blue (Exp. 44).

Acids may cause tendering, if at any time the material is allowed to dry while it contains even a trace of sulphuric or hydrochloric acid.

Other Bleaching Processes. — There are bleaching processes in which the action of the bleach liquor is accelerated by the addition of acetic acid to the solution, which liberates hypochlorous acid, or by passing the damp goods through a chamber containing carbon dioxide.

In electrolytic bleaching processes, the bleach liquor is prepared by the electrolysis of solutions of sodium chloride, or of sodium and magnesium chlorides.

LINEN

The raw linen fiber contains a much larger amount of foreign substances than cotton. While ordinary cotton loses only about 5 per cent, linen loses from 25 to 30 per cent in weight during bleaching, the loss consisting in wax-like substances and pectic matters. The bleaching of linen is a longer and more tedious process than cotton bleaching; while the process, in general, is similar, weaker reagents must be used, as a severe treatment would result either in a tendering of the fiber, or in causing it to be permanently yellow ("setting" the color). Some of the operations must be repeated several times before a satisfactory white is obtained.

Linen Yarn. — The following is an example of a linen bleach: —

(1) *Ley boil*, with sodium carbonate in low-pressure kiers, and wash.

(2) *Chemicking.* — The yarn is reeled for an hour in chloride of lime solution at $\frac{1}{2}°$ Tw. In reeling the skeins are hung on poles which receive an alternate backward and forward rotation, and only a part of the yarn is immersed in the liquid. Wash.

(3) *Sour* with sulphuric acid, and wash.

(4) *Scald* by boiling with soda ash. Wash.

(5) *Chemic* as before. Wash.

(6) *Sour*, and wash.

This gives a half bleach. For a three-quarter bleach, the yarn is (7) *scalded*, (8) *grassed*, by exposure in fields for about a week, (9) *chemicked*, (10) *soured*, and washed. For a full bleach the latter operations are repeated two or three times. The strength of linen yarn decreases the more thoroughly it is bleached.

Hydrogen peroxide will probably bleach linen with less weakening. The methods are the same as for wool.

Linen Cloth. — An outline for a linen-cloth bleach is as follows: (1) lime boil; (2) sour; (3) ley boil; (4) ley boil; (5) grass; (6) chemic; (7) sour; (8) scald; (9) grass; (10) chemic; (11) rub on boards, to remove black specks; (12) grass; (13) chemic; (14) sour.

Jute Bleaching. — Jute may be bleached by treatment first with a warm solution of bleaching-powder, and then, after washing, with dilute sulphuric acid. The material is then washed. If a lighter color is desired, the treatment is repeated with weaker solutions.

Another method is as follows: Pass the goods through a bath of 1 per cent silicate of soda, heated to about 70° C., wash, and then immerse in a bath of sodium hypochlorite containing not more than 1 per cent of available chlorine. The duration of the immersion depends on the grade of jute to be bleached; wash, and pass through hydrochloric acid at $\frac{1}{2}°$ Tw., and wash thoroughly. A still lighter color is obtained if the goods are next passed through a bath containing about 2 per cent sulphurous acid, free, or in the form of sodium bisulphite.

CHAPTER XII

WOOL AND SILK SCOURING AND BLEACHING

Washing Loose Wool. — Loose wool usually contains from 30 to 80 per cent dirt, suint, and yolk. The thorough removal of these impurities is absolutely necessary before the wool can be made into yarn, since it is extremely difficult to remove them from yarn. Imperfect scouring leads to defects in dyeing. The operation of *washing* or *scouring* is very simple. The wool is washed with a warm solution of soap, which dissolves the fats and carries off the waxes in the emulsified condition. Three successive soap-baths are usually used. The wool is rinsed, squeezed, and dried.

Methods and Machinery. — The best results are obtained with a neutral, soft soap, and temperatures not above 35° C. Too high a temperature causes the wool to be harsh. For low-grade wool a cheap soap is often used, sometimes with the addition of sodium carbonate or sodium silicate; or sodium carbonate with no soap. The amounts of soap or soap and soda to be used depend upon the condition of the wool. Pitchy wool requires more than ordinary wool.

The wool may be washed in a wooden vat provided with a false bottom. It is stirred with poles. One type of machine consists of a rectangular iron tank, provided with a false bottom and an automatic arrangement of forks or prongs by which the wool is made to pass slowly from entrance to delivery end. The forks are attached to a frame, which makes a forward stroke in the water, then a backward stroke in the air, and so on; thus setting up a circulation of suds which carries the wool forward. At the delivery end the wool is squeezed by a pair of squeezing rollers. The dirt collects below the false bottom of the tank.

Three of these machines may be used; in order to save soap, the suds from the squeezing rollers on the last machine, which are comparatively clean, are used in the second one, and then in the first, when they are allowed to run off.

Drying machines used are similar to those used for drying cotton (Chapter XIII). Too high a temperature in drying injures the quality of the wool.

Soaps. — Soaps are made by boiling fats or oils with caustic soda or caustic potash, or their carbonates. The best soap for wool washing is a soft soap made with potash. Such a soap is readily soluble in water, and easily washed out. Soap which contains resin should be avoided, as it gives a disagreeable odor, makes the fiber yellow and sticky, and may give rise to uneven dyeing afterward, since the resin is difficult to remove by washing. Soap containing free caustic alkali (sodium or potassium hydroxides) tenders the wool, but this can be prevented by the addition of ammonium carbonate or some other ammonium salt, which reacts with the alkali to form ammonium hydroxide.

By-products. — The waste water from wool washing contains potassium carbonate, wool grease, and soap grease, which it often pays to recover.

Potassium Carbonate. — From 1 to 8 per cent of potassium carbonate (average about 3½ per cent) can be recovered from raw wool. When this is to be recovered, the raw wool is extracted with warm water before being scoured with soap. The watery extracts are evaporated to dryness, and calcined in specially constructed furnaces. In extracting with water, five or six vats may be used, so arranged that water can flow naturally from the first to the second, and so on. The raw wool in baskets is placed, first in the dirty water in the bottom vat; after a short time the baskets are transferred to the next vat, a fresh lot being placed in the first, and so on until the wool passes through the clean water in the top vat. As the water passes down, it becomes more and more impure. This is called the *counter-current* system, and economizes water, and, necessarily, fuel for evaporating it. A similar system is employed in the hank yarn-washing machine (Chapter XIII).

Wool grease. — The fat from the wool and the soap in the water from wool washing may also be recovered. The waste water is collected in large tanks and the dirt allowed to settle. The water is then treated with sulphuric acid, which decomposes the soap, and the fatty acids rise to the surface, bringing the wool grease with them. The water is strained off through canvas filters, and the grease purified by pressing it through sheets of canvas, melting it, and allowing the impurities to settle. It is used as a lubricant, and in cold climates for smearing sheep.

Other Methods of Wool Washing. — Treatment of the wool with a volatile solvent, to remove wool grease, and then with water to remove suint, has been tried, but finds little application on a large scale. The solvents used are carbon bisulphide, benzene, toluene, and petroleum ether. The wool grease is recovered by distilling off the solvent, and the latter is used over again.

Yarn Scouring. — Woolen and worsted yarns usually contain 2 to 6 per cent oil added to prevent the yarn from breaking during spinning. Shoddy yarns may contain 15 per cent oil. The oil is usually removed by scouring before dyeing or bleaching; with cheap blacks the scouring is sometimes omitted.

Some wool yarns curl when wetted, and before scouring, such yarns must be *stretched* to prevent them from becoming entangled during the operation. The yarns are tightly stretched in a frame between pairs of iron rods and immersed in boiling water for half an hour, removed, and allowed to cool. The skeins then are turned halfway around and again treated with boiling water. This process takes advantage of the *plasticity* of wool at high temperatures.

Methods and Machinery. — The yarn scouring is best done in a solution of soap, or of soap and soda heated to 35–45° C. The procedure varies in different works. For the best grades of wool only a good soap is used. The methods are as follows: —

(1) The hanks are hung on sticks as in skein dyeing and turned two or three times in the soap solution contained in an ordinary dye-vat, about a hundred pounds being scoured at a time. They are washed in the same way and hydro-extracted.

(2) A hank is placed in the warm soap solution, allowed to soak while a second is being turned, is turned, and thrown

on a traveling apron which carries it between a pair of squeezing rollers. It is then washed, squeezed, and dried.

(3) The hanks are tied loosely together, end to end, to form an endless belt, which is caused to circulate through the soap bath by means of squeeze rollers. The machine resembles the *dolly*.

By-products. — The wash waters from yarns may be treated like the water from loose wool to recover the soap grease.

Cloth Scouring. — In the manufacture of plain goods it is not usual to scour yarn before weaving. For common black or heavy woolens, the cloth is frequently mordanted and dyed without scouring. Low-grade black worsteds are simply washed in soda. For better-class blacks, and for pieces to be dyed in colors, the material is scoured in soap or soap and soda.

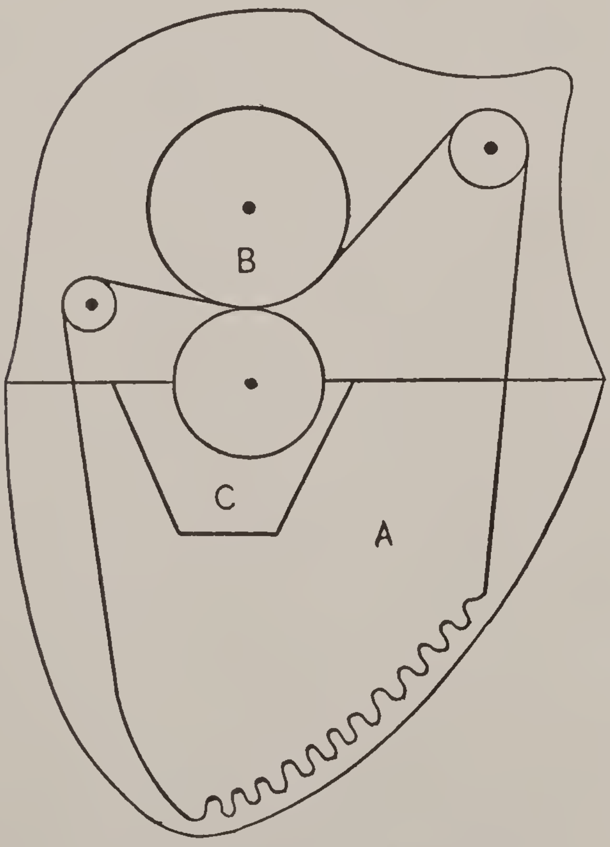

FIG. 8. — Cloth-scouring machine.

There are two kinds of scouring machines. In the *dolly* (Fig. 8) the pieces, sewn together to form an endless chain, are made to pass in the form of a loose rope through the vessel (*A*), which contains the solution of soap, and between two wooden rollers (bowls) (*B*). The bowls draw the pieces through the liquid, at the same time expressing the dirty wash water from them, which flows off in a trough (*C*) below the lower bowl.

The "broad washing" machine is similar to the dolly, except that the pieces pass through the rollers in the open width. It is used for pieces which are liable to crimp or crease if scoured in the rope form.

Crabbing. — Wool cloth made from mixtures of different classes of wool and goods of mixed cotton and wool become uneven when brought in contact with water on account of the different degree of contraction between the two fibers. To prevent this, they must be *crabbed* before dyeing.

The cloth passes at full breadth, and under considerable tension, through boiling water, is wound tightly on a roller, and allowed to cool. The operation is repeated. The cloth is then wound tightly on a perforated iron cylinder, into which steam is admitted. After cooling, the cloth is wound on a second cylinder, and the operation repeated, so that all parts of the cloth will be equally subjected to the action of the steam.

Wool Bleaching. — The bleaching of wool is an entirely different process from the bleaching of cotton and linen. Wool would be completely destroyed in any process of cotton bleaching. In bleaching, the wool is first scoured carefully. It can then be bleached in two ways: (1) by sulphurous acid; (2) by hydrogen peroxide.

Sulphur Bleach. — In wool bleaching sulphurous acid converts the coloring matter to a colorless body, either by reducing it or by uniting with it directly. The change is not permanent, for bleached wool treated with alkaline substances, like soap or soda, becomes yellow again. The bleaching is effected by *stoving*, or by the use of solutions of sulphurous acid or sodium bisulphite.

Stoving. — The stove consists of a small brick or stone chamber lined with wood, which can be closed air-tight. All iron and other metals must be excluded, as they are soon destroyed. *Skeins*, in a damp condition, are hung on wooden rods. About 6 pounds sulphur per 100 pounds of wool are placed in the chamber, and set on fire, and the chamber is closed. After being exposed to the sulphur dioxide 6 or 8 hours, or over night, the skeins are removed and aired. *Pieces* may be bleached in a continuous form of apparatus. They are sewn together, and pass through a narrow slit in the side of the stove, then many times up and down over wooden rollers, and finally out again.

Hydrogen Peroxide Bleach. — Hydrogen peroxide is coming into favor as a bleaching agent for wool. It oxidizes and destroys the coloring matter, and produces a permanent bleach. The bleaching bath may be prepared from commercial hydrogen peroxide, or from sodium peroxide.

Hydrogen peroxide, H_2O_2, comes on the market as a 3 per cent solution in water. It may be adulterated with oxalic acid.

The bleaching bath is prepared by diluting the solution with 5 to 15 volumes of water, and then making alkaline with ammonia or water-glass (sodium silicate). Ammonia is best, as sodium silicate is said to give the wool a harsh feel.

The more alkaline the bath, the quicker its action; but oxygen is evolved from a bath which is too alkaline. The wool is entered into the cold solution, and the bath is gradually heated to 54° C. Lead pipes should be used for heating; and iron and other metals in any form should not be present in the bath, as they cause decomposition of the hydrogen peroxide. The bleaching lasts from 3 to 8 hours. The wool is then soured with a $\frac{2}{10}$ per cent solution of hydrochloric or sulphuric acid, and rinsed. If the bath is heated to a higher temperature, bleaching takes place more rapidly, but more hydrogen peroxide is consumed.

Sodium Peroxide, Na_2O_2, is a pale yellow powder, which is decomposed if exposed to the air, being converted into sodium carbonate. It should be kept in well-closed vessels.

When treated with water, it yields hydrogen peroxide:—

$$Na_2O_2 + 2\ H_2O = 2\ NaOH + H_2O_2.$$

But in the presence of the sodium hydroxide, the hydrogen peroxide is decomposed almost as rapidly as formed:—

$$H_2O_2 = H_2O + O.$$

If sulphuric acid or some other acid is present, decomposition does not take place:—

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$

Sodium peroxide is liable to set fire to paper or other combustible matter with which it comes in contact. It is 13 or 14 times as strong as commercial hydrogen peroxide.

For bleaching with sodium peroxide, sulphuric acid is first added to the bath,—from 7 to 14 pounds per 100 gallons of water. Sodium peroxide (5 to 10 lb.) is next added, with thorough stirring, until litmus paper is just turned blue, and the bath is then made acid with sulphuric acid. Ammonia or sodium silicate is then added, until the litmus paper begins to turn blue again. If the bath contains any sodium hydroxide, or is too strongly alkaline, the wool will acquire a yellow tint, which it is afterward next to impossible to bleach out. The bleaching is conducted as with hydrogen peroxide.

Control of the Bath. — The method is illustrated in Experiment 58 (B). After titration, the strength of the bath can be restored by suitable additions of hydrogen peroxide, or sulphuric acid and sodium peroxide.

EXPERIMENT 58. — Add 5 g. sulphuric acid to 1000 cc. water, stir well, and add slowly 4 g. sodium peroxide. Write reaction. Don't leave any sodium peroxide in contact with paper. (Why?) Stir the solution thoroughly, and test it with litmus paper. If it is alkaline, make it slightly acid with sulphuric acid, and then add ammonia until it is faintly alkaline. Save part of the solution (Solution 1) for (B). Bleach two 5-gram skeins of wool in 400 cc. of the solution, boiling very gently for 30 minutes. Save the solution (Solution 2) for (B).

(B) Dissolve 3.2 g. pure dry potassium permanganate in exactly 1000 cc. water. Measure out 25 cc. of Solution 1 with a pipette, acidify with dilute sulphuric acid, and dilute to about 100 cc. with water.

Titrate the solution with the permanganate from a burette, adding it slowly and with constant stirring until a faint pink color appears in the solution. The beaker should be put on a white sheet of paper. Titrate 25 cc. of Solution 2 in the same way, and calculate what part of the hydrogen peroxide has been consumed in bleaching.

Example. — Solution 1 (25 cc.) required 30 cc. permanganate, and Solution 2, 5 cc. Then $\frac{5}{30}$ or $\frac{1}{6}$ of the hydrogen peroxide remains after bleaching, and $\frac{5}{6}$ have been consumed.

Silk. — Raw silk is deficient in brightness, and generally has a coarse appearance and a harsh feel. It has to undergo various treatments, according to the requirements of the case.

(1) *Boiling-off, stripping, or discharging* consists in removing all the silk gum which covers the silk and gums the individual fibers together. The product is a very brilliant silk.

(2) *Half-boiled silk*, or *souple silk*, has only a portion of the silk gum removed. The loss is from 6 to 8 per cent instead of 20 to 30 per cent as in the previous operation. The silk loses less in weight, but is less brilliant.

(3) *Ecru silk* is raw silk which has been prepared for dyeing by removal of the fatty and wax-like impurities. It has a harsh feel, is not very bright, but is much stronger than boiled-off silk.

Methods of Boiling off. — Boiling off requires two operations: —

(1) *Boiling off the Gum.* — This operation removes the silk gum which covers the thread. It consists in working the silk in a soap bath near the boil, containing 25 to 35 per cent of the weight of the silk of a good, neutral soap. The operation requires about an hour, and furnishes the *boiled-off liquor* always used, if possible, as an addition to the dye-bath for dyeing silk. Hard water should be purified. The silk is removed and washed, if necessary, in a weak solution of soda.

(2) *Scouring.* — By this process the last trace of any impurity which may remain from the preceding operation is removed. The silk is inclosed in a coarse bag

and boiled for $\frac{1}{2}$ to 3 hours in a bath containing 10 to 15 per cent neutral soap. The silk is taken out, washed thoroughly, and dried.

Silk is boiled off as yarn, and in the form of cloth.

Souple Silk. — The operations are as follows: —

(1) *Scouring.* — The silk is worked for about an hour in a lukewarm bath containing 3 to 4 per cent soap and $\frac{1}{2}$ to 1 per cent crystallized sodium carbonate (soda crystals). Fats and oils are removed, and a part of the silk gum.

(2) *Smoothing or Soupling.* — The silk is passed through a bath of boiling cream of tartar, about 4 per cent of the weight of the silk. It is then washed well. This treatment softens the silk, which otherwise has a harsh feel.

The tartar bath can be used continuously. If the souple silk is to be bleached, after scouring and before smoothing it is *stoved*, or bleached with sulphur dioxide in the same way as wool. It may also be bleached with a dilute solution of aqua regia, and then stoved. Souple silk is bleached with hydrogen peroxide after it is soupled.

Ecru silk is simply scoured as in (1) above to remove fats and oils.

Bleaching. — Silk is bleached, like wool, with sulphurous acid. Hydrogen peroxide (or sodium peroxide) is also used for silk bleaching. The methods are the same as for wool. For boiled-off silk, the bath is not heated.

Other Operations. — Silk is subjected to other operations to increase its length or luster. In *stretching*, the skeins are suspended on a stout wooden peg, and stretched by means of repeated jerks on a stout wooden stick placed inside the skein. For *glossing*, the skeins are twisted up very tight, and allowed to remain so several hours. In *lustering*, the skeins are stretched and steamed at the same time.

Weighting of Silks. — Silk has the power of taking up tannic acid and various metallic bodies to a remarkable extent, with a corresponding increase in weight, and without loss in brilliancy. As silk is expensive, advantage is often taken of this property for the production of weighted silks, and silk may be weighted as much as 200 per cent. The weighting may take place before or after dyeing.

For light-colored silk, the following processes are in use: —

(1) *With Tannic Acid.* — After dyeing the silk is washed, and soaked in a cold solution of tannic acid; it gains 12 to 15 per cent in weight, and loses somewhat in brightness.

(2) *With Stannic Chloride* (tin spirits). — The raw silk is repeatedly soaked in a solution of stannic chloride, and washed with water; it may gain in weight up to 25 per cent by repeated operations. Repeated soapings at the boil are necessary to restore the natural feel to the silk.

(3) *Zinc-phosphate-Silicate Method.* — The silk is treated with a solution of stannic chloride (pink salts), then with sodium phosphate, and finally with sodium silicate. A mixture of stannic phosphate and silicic acid is deposited on the fiber. By repetitions of the process, silk can be weighted up to 150 per cent or higher, without injury to its luster or feel. But it loses in strength, and often rots without any apparent cause.

For dark shades or black, silk is weighted: —

(1) With impure *tannins*, as sumac, myrabolans, at an elevated temperature.

(2) *With Ferric Tannate.* — The silk is worked alternately in solutions of tannic acid (in the form of chestnut extract, myrabolons, etc.), and pyrolignite of iron, and exposed to the air after each treatment to oxidize the ferrous tannate first formed. The operations are repeated several times. Another method is to impregnate the silk alternately with a ferric salt and tannin. Silk is weighted in black dyeing up to 200 per cent by this method. The silk must be soaped, and brightened with an acid.

(3) *With Basic Ferric Salts.* — The silk is impregnated with "nitrate of iron," and worked in a boiling soap bath to fix the ferric hydroxide. The operation is repeated seven or eight times if necessary. "Nitrate of iron" is a basic ferric sulphate, formed by treating copperas (ferrous sulphate) with nitric acid.

Silks heavily weighted are liable to spontaneous combustion. Other methods of weighting are in use.

CHAPTER XIII

DYEING MACHINERY AND MANIPULATIONS

Cotton and wool are dyed in the form of loose cotton or wool; as slubbing or sliver; as yarn in skeins and warps; and as cloth. Cotton, in addition, is dyed in the cop. Silk is dyed as yarn or cloth. These different forms necessitate the employment of different kinds of machinery and different modes of handling.

Raw Stock. — Loose cotton or wool is dyed for the production of colored filling; also to make fancy yarns of different kinds. Loose cotton or wool of different colors is sometimes mixed to produce some desired shade. A dark color reduced by mixture with white material produces a faster shade than one in which all the cotton is uniformly dyed.

The production of even colors is of no great importance in dyeing raw stock, as any inequalities are removed by the mixing which occurs in the different processes of manufacture. The dyer should endeavor to keep the loose material as open as possible, as any matting of the fibers causes considerable loss in subsequent processes. Dyed cotton has a greater wearing action upon the teeth of the carding machine than undyed cotton.

Dyeing. — Raw stock may be dyed in plain vats, being stirred with poles. For convenience in handling, it may be placed in nets or baskets.

The machine used for dyeing raw stock may be represented by the Klauder-Weldon dyeing machine (Fig. 9). It consists of a drum of heavy copper netting caused to revolve in a dye-vat, which is heated by steam-pipes. The cylinder is divided into a suitable number of compartments, provided with doors. When dyeing, the drum is set in motion and caused to revolve in the dye-bath until the material is dyed the desired color. This machine can be used for boiling off, bleaching, mordanting, and dyeing.

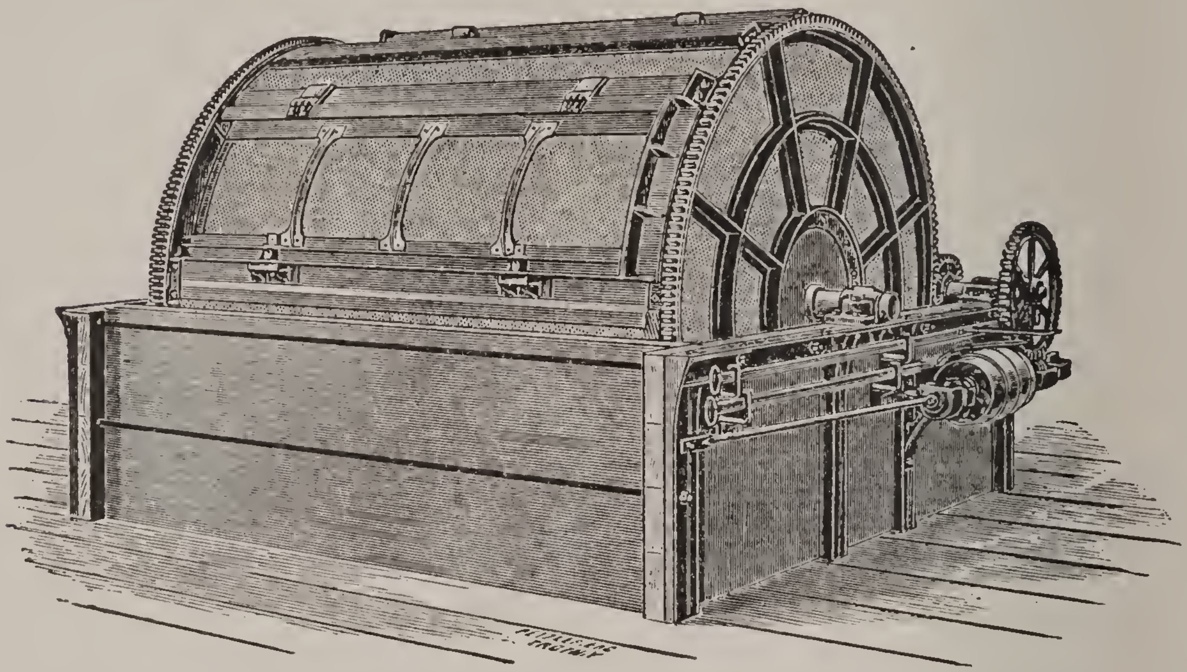

FIG. 9. — Klauder-Weldon raw stock dyeing machine.

Washing. — The washing may be performed in the same vessels as are used for dyeing, or in the hydro-extractor.

Drying. — The excess of water is first removed by squeeze rolls, or a hydro-extractor (see under Skein Drying). Sometimes cotton is next passed through an opener, so that it will come to the drying machine proper in a perfectly loose condition.

There are two types of dryers. In one type the raw stock is placed upon shelves of galvanized iron wire netting, in drying chambers, which are heated directly, or by hot air which is blown through by fans. The air may be heated by steam, or the chamber may be placed over the boilers of the plant.

In another form of drying machine (Fig. 10) the cotton is fed into a hopper (*A*) at one end, on to an endless wire apron (*B*), which carries the cotton through successive chambers, and delivers it dry at the other end. The drying chambers are at a moderately high temperature at the wet end, and grade to a lower temperature at the point of exit. Air is blown through the machine by suitable fans (*C*).

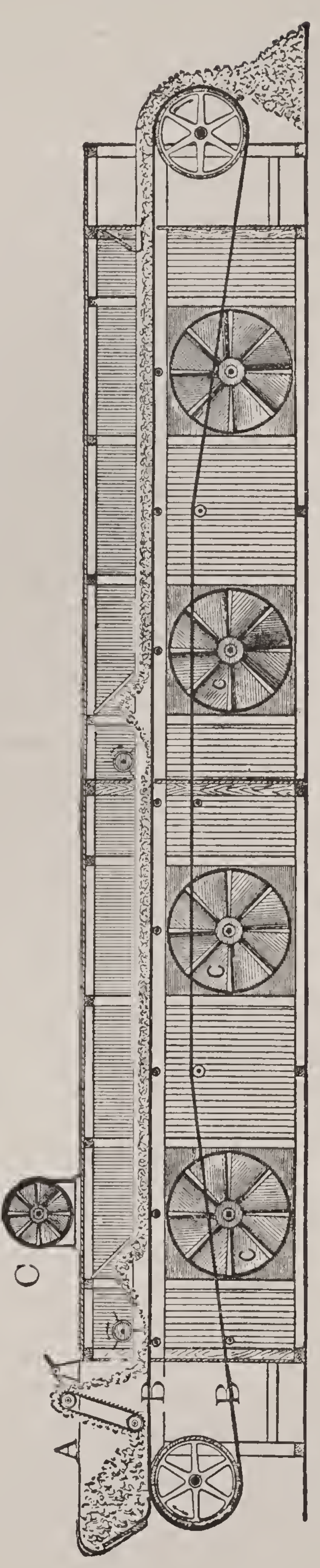

FIG. 10. — Raw stock drying machine. (Philadelphia Textile Machinery Co.)

Sliver or Slubbing. — The object of dyeing carded cotton in the form of sliver or slubbing is to produce the effects of raw stock dyeing and avoid the action of the dyed cotton on the cards and the loss due to matting of loose cotton during the dyeing process.

Wool slubbing is dyed for the production of fancy yarns.

Sliver or slubbing is placed between two perforated metallic plates or cylinders, and the dye liquor is sucked through it by means of a pump.

Wool slubbing and "tops" are also reeled off into skeins, and dyed in skein-dyeing machines.

Skeins. — The object of yarn dyeing is to produce figured designs by weaving colored threads into the cloth. Skeins and cops, as a rule, are used for filling. Skeins are dyed more easily than yarn in other forms. Skeins are dyed by hand or by machinery.

Hand Dyeing. — A round tub is employed in some forms of hand dyeing, but the ordinary form of dye-vat is rectangular. Vats for dyeing cotton are made smaller than for the same quantity of wool.

Plain vats or tubs are used for dyeing and otherwise treating goods cold, or at a lukewarm heat, when a supply of hot water is provided. When, however, it is necessary to work at or near the boil, the vat must be heated with steam. A steam-pipe is placed in the bottom of the vat, with a perforated false bottom above it, to prevent the material to be dyed from coming in direct contact with it. The pipe is usually of copper, sometimes of iron, tin, or lead. The pipe usually passes down one corner of the vat, which is also boxed off. Dark stains or stripes on goods are sometimes due to their coming in direct contact with the steam-pipe. If one portion of the bath is hotter than other portions, the dyeing may not be uniform.

The vats are usually heated by direct steam, the pipe being perforated so that the steam can pass directly into the bath, causing a good circulation of the liquid in it. Some of the steam is condensed, and dilutes the dye-bath, but the quantity condensed hardly more than counterbalances the water lost by evaporation and that removed with the goods. In some cases, however, it is best to heat the bath with a closed steam coil, thus preventing its dilution. The water condensing in the coil may be collected and used for preparing the dye-baths.

When direct steam is used, it is essential that the steam should be clean and free from particles of oil. Impure steam usually results in spots or stains on the dyed goods.

The skeins are hung upon sticks, usually made of hickory, but ash, beech, or any hard wood that does not swell much when treated with water may be used. A pole made of a sapling with all the bark removed and the branches lopped off is preferred.

The Operation. — The dye being fully dissolved, a stickful of skeins is placed in the vat, lifted two or three times to wet the skeins, and placed in the vat with the ends of the sticks resting on its edges. After all the skeins have been entered in the same way, the skeins are "turned." The sticks are arranged so as to be about four inches apart, and a foot from one end of the vat. Two men lift a stick full of yarn, one puts a short stick through all the skeins, the one on the other side grasps it and lifts it, thus giving the yarn a quarter turn. The stick is placed close to the end of the vat, and the others are turned in the same way. "One turn" has then been given. The dyer gives three or more turns, as may be necessary.

Machine Dyeing. — Various machines have been constructed for dyeing skeins. One form is the Klauder-Weldon skein-dyeing machine (Fig. 11).

On a central axis are built two disks or rod carriers, which can revolve in the dye-vat, the revolution being given by suitable gearing, which is shown at the side of the machine. On the outer edge of the disk are clips for carrying rods, on which one end of the skein of yarn is hung, while the other end is placed on a similar rod carried near the axle. The revolution of the disks carries the yarn through the dye liquor, and at a certain point the rods carrying the yarn are turned.

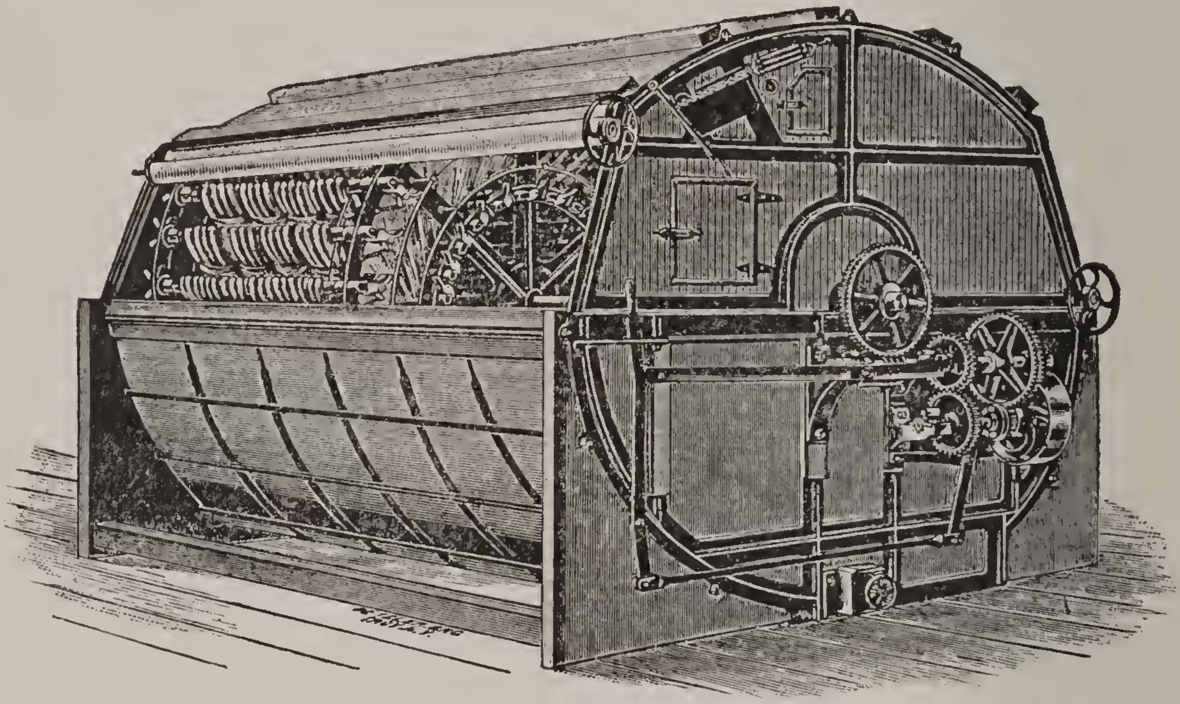

FIG. 11. — Klauder-Weldon skein-dyeing machine.

In another form of skein-dyeing machine the yarn is hung in a vat on dye sticks, or reels, which are caused to revolve by suitable gearing.

A third machine lifts the skeins, turns them, and puts them back in the vat; its action resembling hand dyeing.

Washing. — Skeins may be washed by hand in dye-vats, the operation being the same as dyeing.

Washing machines for single skeins are constructed according to two principles.

In the first type, the skeins are hung on sticks or rollers, which are caused to revolve by suitable gearing, while the skein hangs in a vat of water. Fresh water flows in at the top and the dirty water flows off at the bottom.

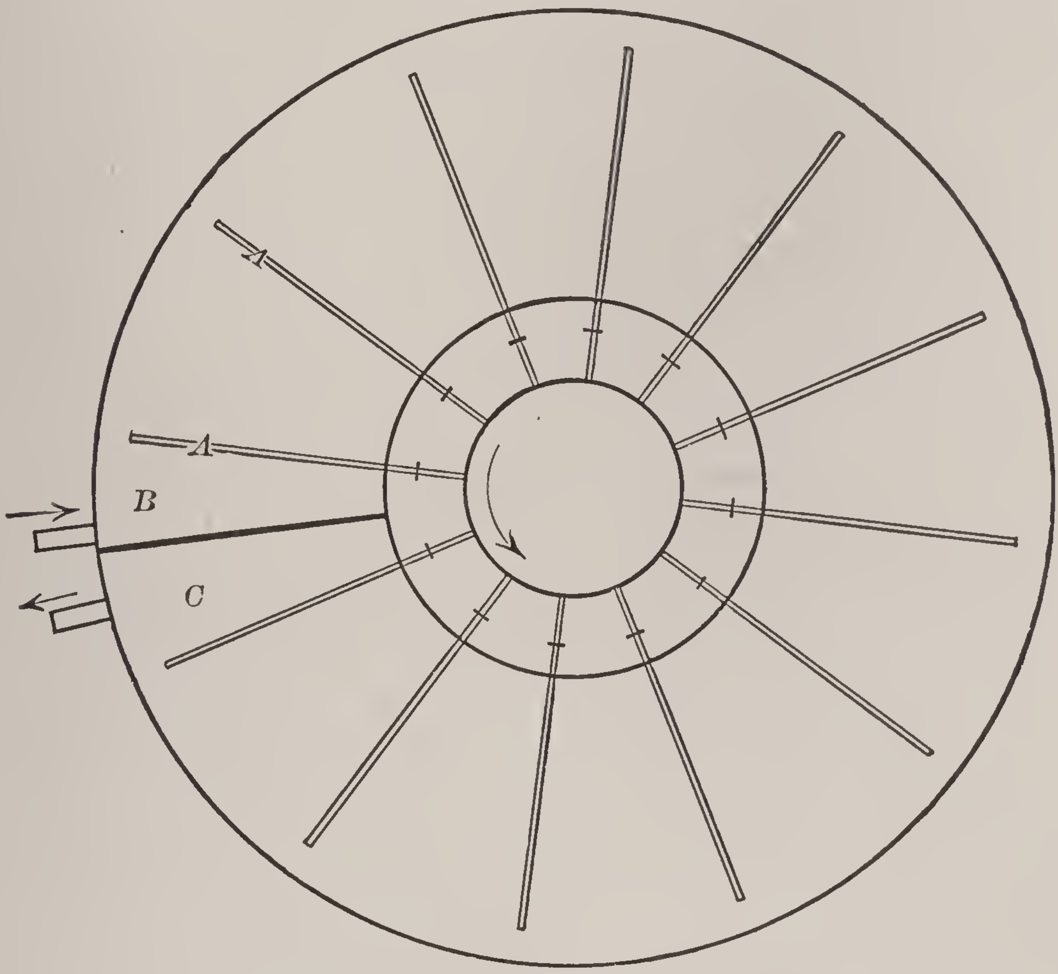

FIG. 12.—Skein-washing machine.

In the second type (Fig. 12), the skeins are hung on sticks (*A*) or rollers, which revolve, and at the same time move from one end of the vat to the other. The vat in the figure is circular so that a single man may handle the washed and unwashed skeins. Clean water flows in where the washed skeins are taken out (*B*), and the dirty water flows off near where the unwashed skeins are entered (*C*). The skeins thus move in a direction opposite to the flow of water — the *counter-current* system, as it is called.

Extracting Water. — Excess of water may be removed from skeins in three ways: wringing, squeezing, and hydro-extracting.

In wringing, the skein is hung on a hook or short stick driven in the wall, and twisted by hand by means of a short stick. The skein is turned around, and the operation repeated. Wringing machines are used in some branches of dyeing.

In squeezing, the skein is passed between two rollers, which are pressed together by means of a spring, or a lever and weights.

The hydro-extractor, or "whizzer" (Fig. 13), as it is called, consists of a perforated basket of copper, or galvanized iron, arranged in an outer cover so that it can be revolved at a high rate of speed. The goods are placed in the basket, taking care to distribute them as evenly as possible, and the latter set in motion, when the centrifugal force throws the water out of the basket into the outer casing, whence it flows off. The operation is over in about five minutes. Hydro-extractors may be driven by hand power, by belts and shafting, by a small steam-engine attached directly to them, or by an electric motor. The best types of hydro-extractors are provided, as in the figure, with arrangements to minimize the unavoidable vibration which occurs when they are driven. The machine is hung, as a whole, on supports, so that it can vibrate without shaking its foundations.

The relative efficiency of wringing, squeezing, and hydro-extracting is shown by the following table, which gives the percentage of water removed from the goods by the three processes:—

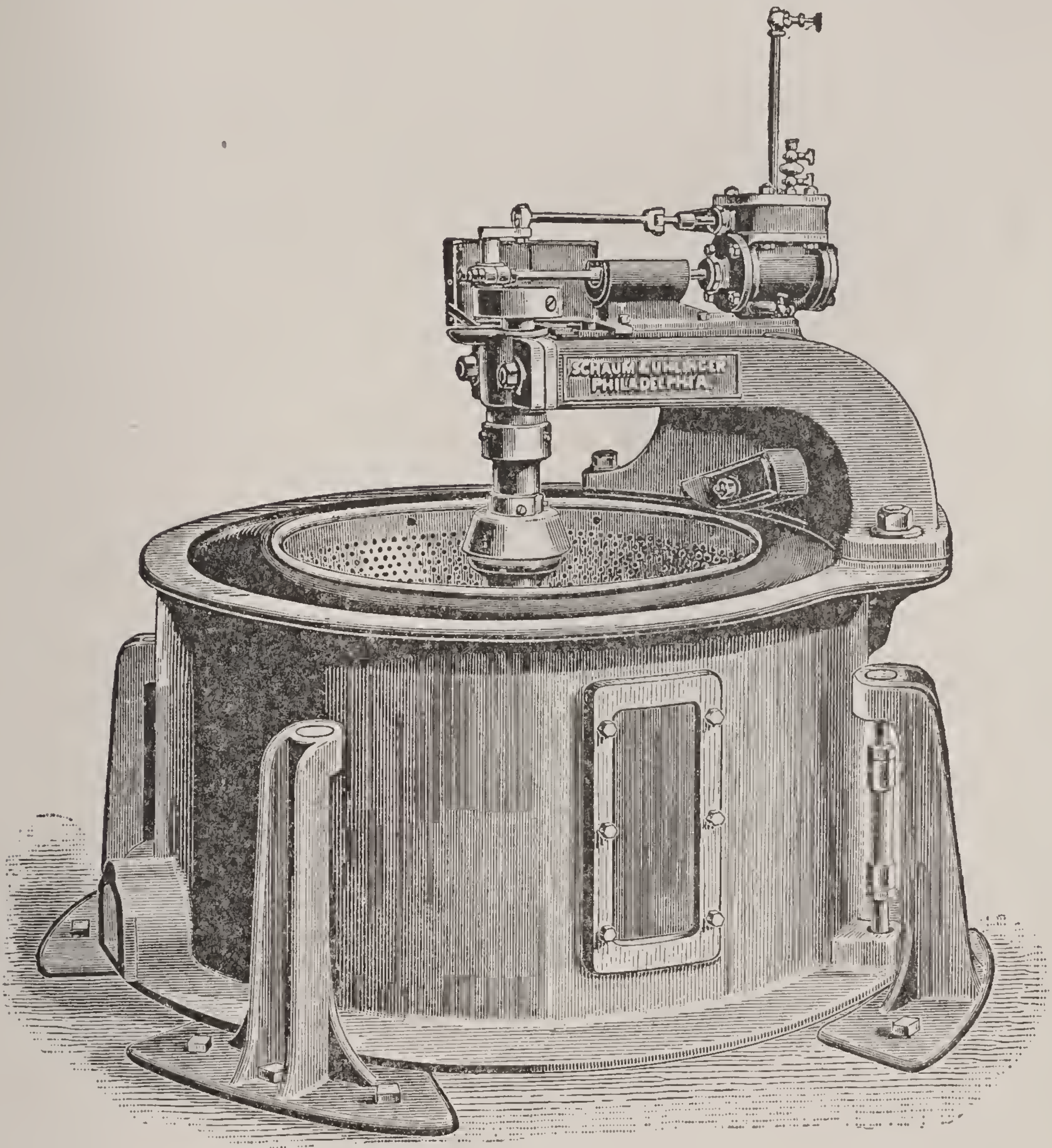

FIG. 13.—Hydro-extractor.

Wringing cotton yarns . . .	45 per cent
Squeezing	72 " "
Hydro-extracting	82 " "

Drying. — After the excess of water has been removed the skeins are dried. They may be placed on sticks, which are placed in a drying oven, a room heated by steam-pipes or hot air, or a continuous machine similar to that for drying loose cotton (Fig. 10) may be used, the skeins hung on sticks being placed on an apron at one end, and taken off dry at the other end.

Warps. — Warps to be dyed may be of considerable length. Sometimes they are doubled several times, but as a rule they are dyed as single warps. The dyeing must be so managed that the warp is of uniform color.

Dyeing Machines. — Warps are always dyed in machines which are the same in principle, though they vary in the form and arrangement of their parts. Figure 14 represents one form. The machine consists of a dye-vat (*A*) provided with suitable heating arrangements, and containing a frame which carries a number of copper rollers (*B*). One or more warps may be dyed at a time. The warps pass from the boxes, on the overhead frame, between the pegs (*E*), and then pass up and down over the rollers (*B*), and finally out between a pair of iron or wooden squeeze rollers (*C*) into a box set to receive them. The apron (*D*) lays the warps evenly in the boxes. The warp has then had "one run." It is given as many more "runs" as may be necessary to produce the desired result. For heavy warps, the number of rollers is increased. The warps are kept separate by guide pegs.

The machine in the figure is arranged for eight warps.

Two or more machines are sometimes arranged in series, so that the warp passes from one vat into the second.

Sizing. — Warps are often sized immediately after dyeing in machines constructed on the same principle as the warp-dyeing machines. The vats are much smaller, however, and only one or two guide rollers are necessary.

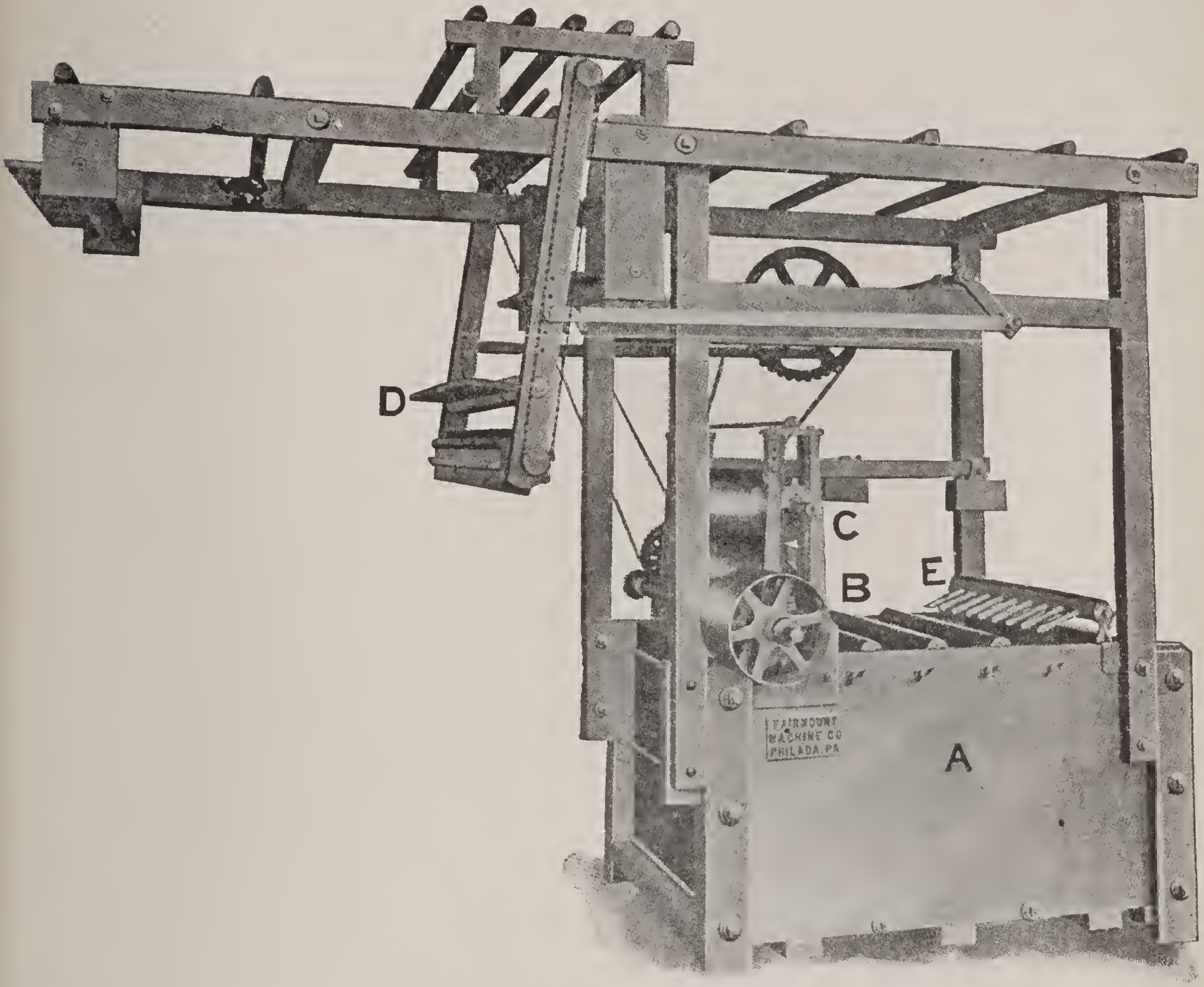

FIG. 14. — Warp-dyeing machines.

Drying. — The warps are squeezed by the dyeing machine. They are next dried, usually on iron cylinders heated by steam, technically termed "cans," or tins (Fig. 15). The warp passes spirally around the outside of the

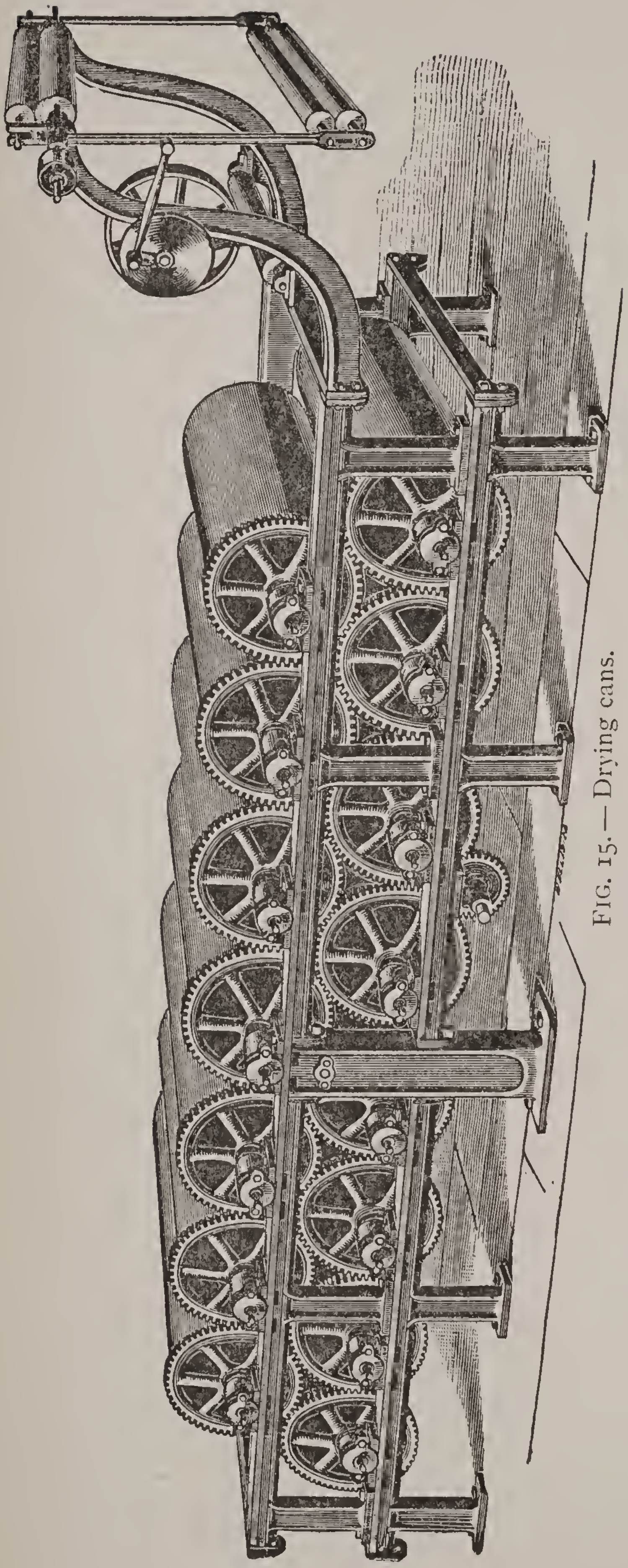

Fig. 15. — Drying cans.

cans, usually passing over from ten to twenty of them. The condensed water from the cans may be collected and used for preparing the dye-bath. The number of cans used varies, and they are arranged in a number of ways, both horizontally and vertically.

Dyeing on the Cop. — The object of cop dyeing is to avoid reeling yarn from bobbins or cops into skeins for dyeing, and reeling it back again. The difficulty in cop dyeing is to secure even penetration, so that the outer and inner layers of yarn will possess the same color. Only very soluble and level-dyeing dyestuffs may be used for cop dyeing.

In the cop-dyeing machines, the cops are placed upon perforated metal spindles, which are so connected with a pump that it sucks the dye liquor through the cop and returns it to the vat. The machines are made in a variety of forms.

Cloth. — Cloth when dyed must possess a uniform color, free from spots and stripes, and the interior of the fabric must be the same color as the exterior.

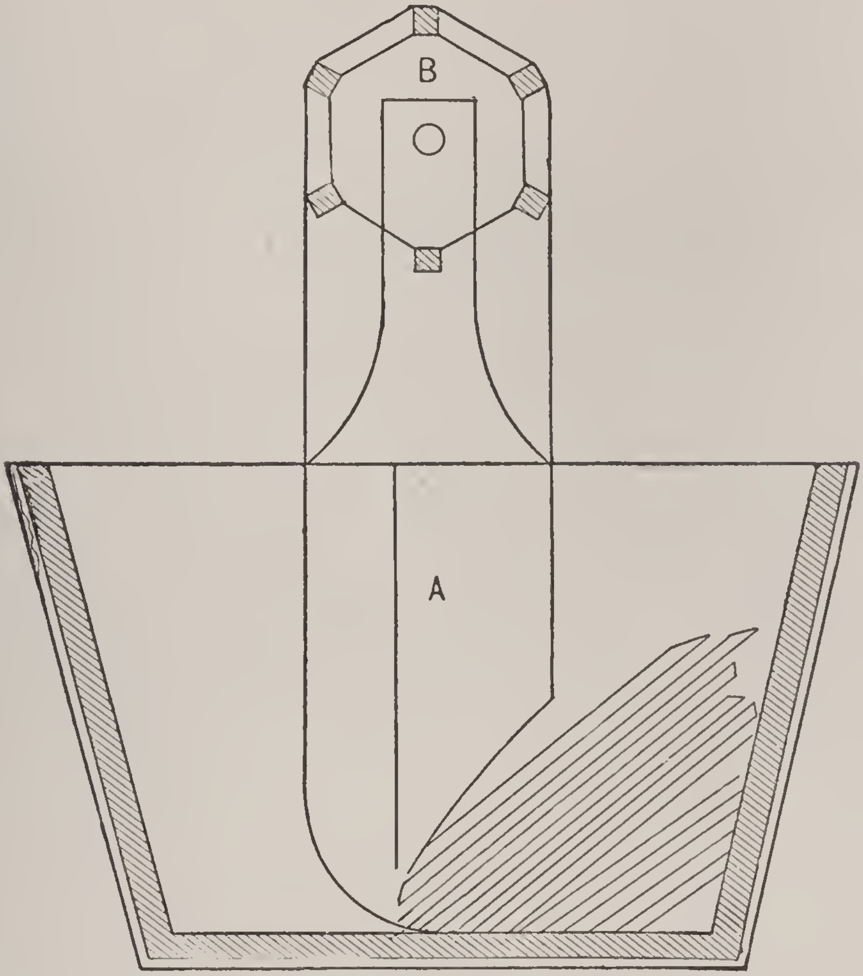

FIG. 16. — Dye-beck and wince.

The dye-beck and wince, the jigger, the padding machine, the hawking machine, and the single-color printing machine are used for cloth dyeing. They vary somewhat in form and size.

The *dye-beck and wince* (Fig. 16) consists of a wooden or cast-iron vat (*A*), over which a wince, or skeleton roller

(*B*), is supported. The vat is divided by a perforated diaphragm, which is open below, in order to allow the pieces to pass freely beneath it. The pieces, stitched together in the form of endless bands, are drawn by the revolution of the wince continuously in the same direction, and are prevented from becoming entangled with each other by means of a series of wooden guide pegs which divide the several pieces.

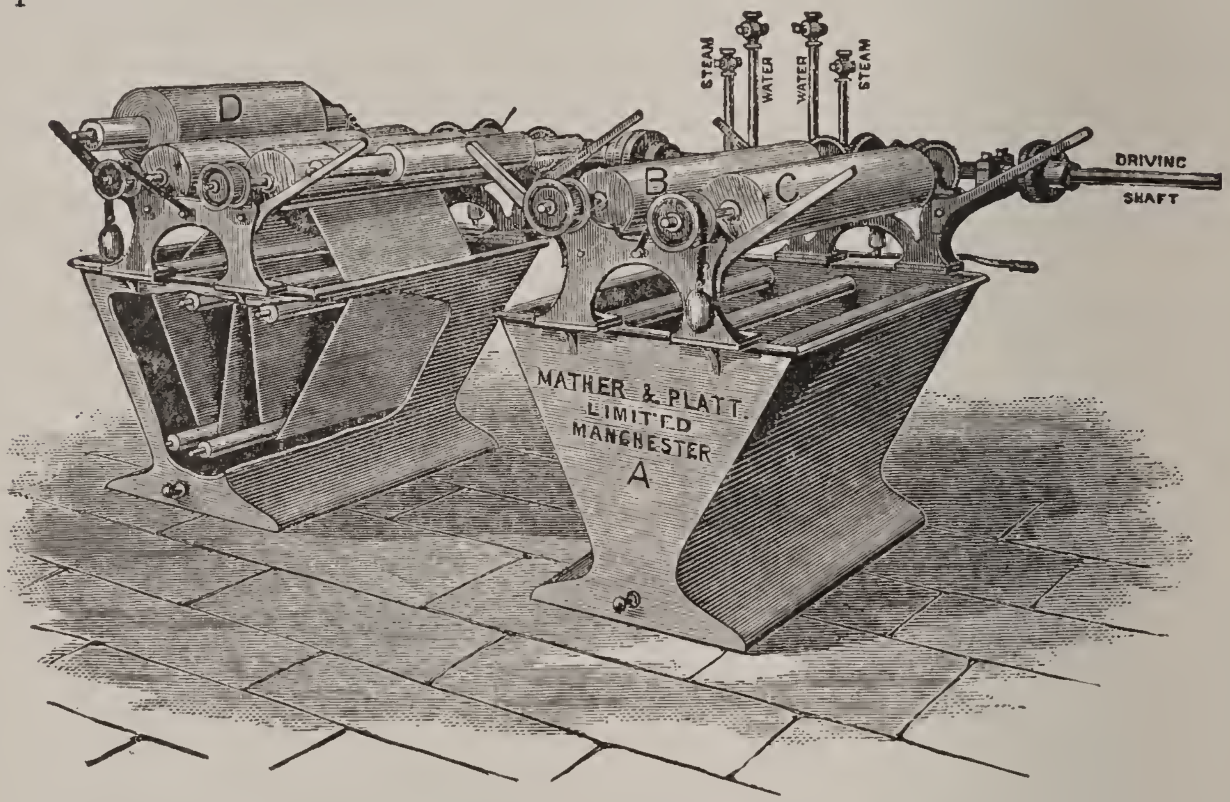

FIG. 17.— Jiggers.

The *jig*, or *jigger* (Fig. 17), consists of a dye-vat (*A*) larger at the top than at the bottom, containing three guide rollers. The cloth is wound on a roller (*B*), passed over the guide rollers in the vat, on to a second roller (*C*). When the machine is set in motion, the cloth is wound from the first to the second roller. The direction is then reversed, and the cloth wound back again, and so on as long as may be necessary. When the dyeing is finished, the cloth is wound on a third roller (*D*) called the *batch roller*, and the operation is called *batching*. For some kinds of dyeing, the jigger is provided with a pair of squeeze rollers to squeeze out the excess of dye liquor before batching.

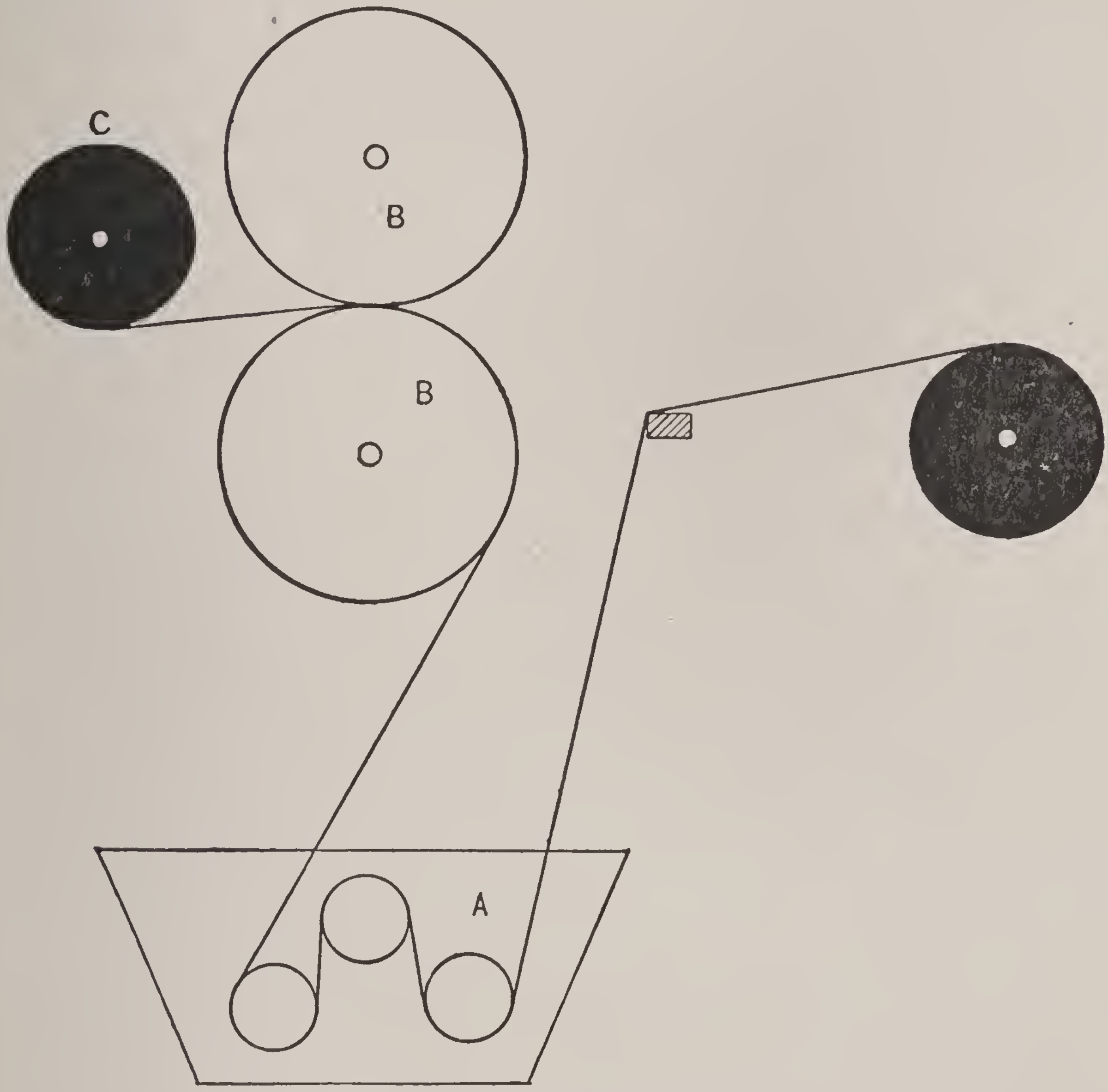

FIG. 18. — Padding machine.

The *padding machine* (Fig. 18) is used chiefly for dyeing light colors on cotton cloth. The cloth passes through the thickened dye liquor contained in the vat (*A*), then between squeeze rollers (*B*), and on to a second roller (*C*). The operation is then finished. The operation really consists in impregnating the cloth with a colored solution and drying it. The depth of color depends upon the strength of the solution, and the pressure of the squeeze rollers.

The *single-color printing machine* (Fig. 19) is used for padding cloth on one side only (*slop padding*). The piece passes around a large iron roller (*A*), which presses against the copper or brass printing roller (*B*). The latter is fed with color by a wooden roller (*C*) which runs in the thickened color or mordant in the color-box (*D*). The surface of the printing roller is engraved with fine lines which take up more or less color according to the depth of the engraving. The excess of color is scraped off the printing roller by a steel blade (*E*), the *color doctor*. Between the cloth and the iron roller is a thick band of felt, called the *blanket*, and a second band usually runs between the blanket and the cloth, to prevent the blanket from being soiled.

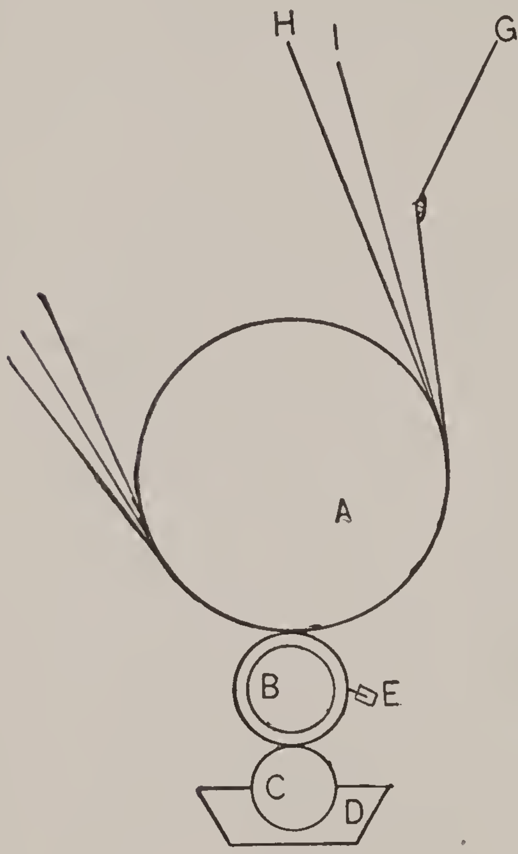

FIG. 19. — Single-color printing machine.

The *hawking machine* is used in the case of dyes which must not be exposed to the air. It consists of a series of guide rollers arranged in a vat so as to be covered by the dye liquor. The cloth is sewed together in the form of an endless belt, and drawn continuously in an open form through the dye liquor by means of a pair of rollers, driven by suitable gearing, and placed beneath the surface of the liquid.

In dyeing with the dye-beck and wince, the quantity of water used must be relatively large in proportion to the amount of goods. A smaller quantity of water and stronger solutions of dye may be used with the jigger.

Drying.—The cloth is squeezed, opened, if necessary, to its full width, and then dried on cans similar to those used for warps. It may also be dried by passing up and down through a hot chamber, emerging dry at the other end.

Printing of Slubbing and Warps.—Slubbing is printed in stripes for the production of certain kinds of yarns, and printed warps are necessary for the production of some classes of figured goods.

The machine used is similar to the single-color printing machine (Fig. 19); as many printing rollers are used as may be necessary. Usually the printing roller is fluted, but any design desired may be engraved upon it. The color remains in the engraved parts of the roller, being scraped from the other parts by the color doctor. The engraving must be much deeper for slubbing than for warps, and the blanket should be softer.

Warps are printed after they are beamed.

CHAPTER XIV

GENERAL OBSERVATIONS ON DYEING

Material which has been properly dyed is of a uniform color in every part, free from spots or streaks of every kind, and with the interior of the fabric the same color as its exterior. For the production of level dyeing, as it is called, every dye and class of dye has its special characteristics and methods of application, which vary with the kind of fiber and the nature of the material. But there are certain considerations which are applicable to every class of dyes, and every kind of dyeing, and it is these which will here be presented.

Dissolving the Dye. — It is essential that the dyestuff should be uniformly distributed through the dye-bath. In the case of insoluble colors, which occur in the form of pastes, the dyestuff is mixed with water, and poured into the bath through a strainer of cloth. Soluble colors, which occur as powders or pastes, must, as a rule, be dissolved very carefully, as undissolved particles will often produce dark spots on the goods, known as *dye-spots*. Boiling water may be used for most dyestuffs, with the exception of certain colors which are decomposed by boiling water and can be dissolved in warm water only. Some few colors require solution in alcohol. The solutions should be poured into the bath through a filter, to catch undissolved particles.

Hard Water. — Hard water is generally injurious in dyeing, as in most cases it precipitates a portion of the dyestuff, either in the form of a calcium salt, or, in the case of basic dyes, as the color base. If pure water is not available, hard water should usually be softened before the dye is added to the dye-bath.

The methods for softening water on a small scale are as follows: —

(1) The water is boiled. This removes temporary hardness only, calcium carbonate being precipitated according to the following reaction: —

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2.$$

(2) The water is boiled with the addition of sodium carbonate. Both temporary and permanent hardness are removed by this method, calcium sulphate being decomposed as follows: —

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3.$$

(3) The water is boiled with the addition of soap. Insoluble calcium salts of the fatty acids of the soap are formed, and appear as a scum on the surface of the water.

In each of the three cases, the boiling should continue for five or ten minutes. The water may be allowed to settle, and be drawn off from the sediment, but this is not always necessary. The amount of softening agents to be used depends upon the hardness of the water.

(4) The water is neutralized or *corrected* with acetic acid (applicable for basic dyes only). The hardness is really not removed, but as the water is no longer alkaline, it will not precipitate basic dyes.

Correction of Water. — A liter of the water to be corrected is poured into a porcelain basin, tinted with methyl orange, and titrated with $\frac{n}{10}$ hydrochloric acid (10 cc. hydrochloric acid 34.2 Tw. per liter of water). The acid is delivered from a burette until the color of the liquid just changes.

The number of cubic centimeters of acid required multiplied by 0.26 gives the number of ounces of acetic acid of 9° Tw. required to neutralize or correct 100 gal. of water.

Other impurities in water cause trouble. Water which contains appreciable amounts of iron cannot be used in dyeing or bleaching without purification. Organic matter in water sometimes reduces a dye, thus leading to defective colors.

Water Purification. — As hard water consumes soap and dye and causes trouble with boilers in many plants, it is economical to install a plant for the purification of water, to be used for boilers, for dyeing, and for wool washing. A thousand gallons of water of 1 degree of hardness will destroy 1½ lb. soap, so if the water used in wool scouring has over 5 to 10 degrees of hardness, the loss of soap will be considerable. The softening is usually accomplished by means of a mixture of sodium hydroxide and calcium hydroxide (slaked lime), which precipitates the calcium salts as calcium carbonate. The apparatus in use varies. It may consist of an upright tank with a number of inclined partitions on which the calcium carbonate may settle as the water rises slowly to the top of the vessel; or the calcium carbonate may be filtered out in a filter press.

Waste water from large dyeing or bleaching establishments should usually be purified before it is allowed to flow off. The methods to be followed depend upon the nature of the impurities.

All the water can be run into a large tank, where many of the impurities precipitate each other; the precipitation may be completed by the addition of slaked lime mixed to a paste with water (*milk of lime*). The water is then allowed to settle, or is filtered, and run off.

Production of Level Dyeings. — In all apparatus used for dyeing, some portions of the material are always less exposed to the action of the dye liquor than other portions, being out of the bath, or protected by folds of cloth, etc. In general, the dye must not be taken up too rapidly by the fiber, or portions of the material will get more than their share. In the jigger, for example, if the absorption takes place too rapidly the first portions of the cloth to pass through will take up the greater part of the dye.

The general methods for retarding the absorption of a dye are as follows: —

(1) *Regulating the Temperature.* — As a rule, the absorption of dyestuffs increases with the temperature of the dye-bath. By entering the goods at a low temperature, and raising the temperature slowly, level dyeing is promoted.

(2) *Regulating the Addition of Dyestuff.* — Instead of making the addition of all the dye at once, it is added in portions to the bath. This method is of advantage in warp dyeing, and in dyeing on the jigger.

(3) *The Proper Use of Assistants.* — Some assistants

cause the dye to go on the fiber more rapidly, while others decrease the rate of its combination with the fiber. By the addition of the assistants at earlier or later stages of the operation, or by increasing or decreasing their amount, the rate of absorption of the dyestuff may be largely controlled.

Special methods required by each class of dyestuffs are given in their proper place.

The rate at which the absorption of dye may safely be allowed to take place depends upon four things: the thickness of the material to be dyed, the depth of color to be produced, the kind of machine which must be used, and the nature of the fiber itself.

Thickness of the Material. — Thick cloth, heavy warps, and tightly spun yarn are less easily penetrated by solutions, and must be dyed at a slower rate than thinner material or soft yarns, which are easily penetrated. Too rapid absorption of the dye leads to deficient penetration, *i.e.* the interior of the cloth or warps will be a lighter color than the outer portions, or the dye may be fixed superficially, and not be fast to rubbing.

Depth of Color. — Dark shades may be dyed more rapidly than light colors, as the large quantity of color present affords all portions a more equal chance to become dyed. Light colors must always be dyed much more slowly and cautiously.

Kind of Machine. — Raw stock does not require level dyeings, as inequalities are removed in subsequent processes of carding and spinning.

Cop dyeing calls for very level dyeing colors, and great precautions in delaying the absorption of the color, to insure an even shade in all parts of the yarn, as yarn on the cop is penetrated slowly by the liquor.

Skeins are comparatively easily dyed.

For the warp-dyeing machine, and the jigger, the color solution must, as a rule, be added in several different portions during the passage of the warp or cloth.

The Fiber. — Cotton has slight affinity for dyes, and in dyeing it with direct colors it requires few precautions for retarding the absorption of the dye. When a mordant is used, the combination takes place between dye and mordant, and the precautions to be used depend on their nature rather than that of the fiber. Wool and silk have such affinity for dyes that it is necessary to prevent them from being absorbed too rapidly.

Feeding of Colors. — When goods are allowed to remain in the dye-bath while it cools down, a further absorption of dye called "feeding" takes place, which is often of advantage, but sometimes is a disadvantage. If the material is piled up, or hung on poles while still wet from the dye-bath, and left too long, the dye liquor will descend to the lowest parts of the mass, and by feeding produce uneven shades. Similar faults result in dyeing with the jigger when the cloth, saturated with the dye liquor, is allowed to remain too long on the batch roller before squeezing or washing.

Standing Baths. — In many processes of dyeing, the dye or reagents are only partly removed from the bath. It is often an advantage when several lots are to be dyed the same color to use the same bath over and over again, restoring its strength each time after using by suitable additions. The use of standing baths, as they are called, saves time in making up a new bath, saves the dye or salts in the old bath, and often saves the time or heat required to raise the temperature of the new bath. Of course, in time the standing baths become dirty and must be thrown away.

Mixing of Dyes. — Comparatively few dyeings are made with single dyestuffs.

Dyes are combined in two ways: by mixtures in the same bath and by *topping* a color with other dyes. For mixing in one bath, dyes of the same class must be used; the methods of topping depend somewhat on the nature of the colors, though basic colors are usually used for topping. The principles of color mixing are given in another chapter.

Dyeing to Shade. — Dyers are usually called on to match a certain color. Matching a given color is called *dyeing to shade.* In dyeing to shade, it is better to start with too little dyestuff in the bath than too much, as a deficiency is easily corrected. When the dyeing operation is nearly finished, the dyer removes a sample of the goods (which may be small pieces of the goods attached to it for that purpose), dries the sample, which alters its color, and compares it carefully with the color to be matched. This is done in two ways: the dyer first holds the two samples side by side between him and the light, and catches the reflection from the material, and then he turns and examines it with his back to the light. If the color is correct, but too light, more of the dyestuff is added, and the operation continued. If the color does not have the correct hue, other dyestuffs are added to the bath; or the color may be *topped* in another bath. Small additions to a dye-bath should always consist of easily leveling colors.

In color matching, the nature of the light is of considerable influence. The best lights are: the light from a northern exposure, an electric arc light, or burning magnesium ribbon. Ordinary gas-light and lamplight are too red to give the correct tone to color.

When the eye has been tired by matching a number of colors of the same shade, it may be rested by looking at the complementary color to those matched.

In matching a color, the dyer must consider the effect of the subsequent operations which the material is to go through. Sizing may affect the color, and cloth is frequently heated or ironed in finishing, which has the effect of changing the shade of a number of coloring matters. For example, some blues have a tendency to become redder, and some yellows are liable to incline toward orange.

Fastness of Dyes. — The methods for estimating the fastness of colors to perspiration (Exp. 9), alkalies (Exp. 10), washing (Exp. 7), boiling water (Exp. 6), rubbing (Exp. 36), and milling (Chapter IX) have already been given. Of course, the best test for any color is practical trial of it.

Fastness to Cross-dyeing. — Dyed cotton which is to be woven with woolen yarn when the latter is to be dyed in an acid bath (as with Biebrich scarlet) must be fast to cross-dyeing.

Test: — Plait the yarn with wool and boil for 20 minutes in water containing 1 gram sulphuric acid per liter, rinse and dry. The extent of bleeding should be noticed.

Fastness to Bleaching. — Colored threads are sometimes woven in cotton goods afterward to be bleached — for example, the headings of towels. The color must be fast to bleaching. Comparatively few dyes stand this test.

Test: — Treat the dyeing for 15 minutes in a solution of bleaching powder at ½° Tw., sour with dilute hydrochloric acid and wash.

Fastness to Stoving. — The color must resist the action of sulphur dioxide. Colored yarns to be woven with wool which is to be bleached with sulphur must stand this test.

Test: — Moisten the dyed material, and place it in a closed vessel with a piece of burning sulphur, for 12 hours.

Fastness to Ironing and Calendering. — Many coloring matters are altered on ironing or drying, though the change in almost all cases is temporary. It may prove troublesome in color matching.

Test: — Press the material with a hot iron, and note any change in shade.

Fastness to Carbonizing. — Test: — Saturate the dyeing with a 5 per cent solution of sulphuric acid, wring out and dry between undyed woolen material at about 92° C., then pass through a 1 per cent solution of sodium carbonate, rinse and dry.

Fastness to Potting. — Dyes which are fast to potting must stand steaming under pressure.

Fastness to Light. — The fastness of a dye to light varies with the material on which the dyeing is made, and on the depth of the dyeing, light colors being affected very much more rapidly than dark ones. The intensity of light varies with the season of the year and the latitude and weather of the place. The fastness of a color to light is to be determined by comparing the sample to be tested with other samples of known fastness exposed at the same time.

Test: — Expose the sample to be tested, dyed a moderately dark shade, to direct sunlight under glass, protected from rain but with free access of air. The exposure should be made facing the south if possible. A sample of the material is preserved in a dark box, for comparison. Expose, at the same time with the sample to be tested, three samples of wool dyed with (*a*) quinoline yellow S or indigo carmine (fugitive colors); (*b*) congo orange R or alkali blue 6 B (moderately fast); and (*c*) chrysamine G or naphthol blue black (fast colors). The samples should be examined every month, and the exposure stopped when one-half of the color to be tested has been destroyed. If this occurs before the color of quinoline yellow S or indigo carmine has been affected, the color is *very fugitive;* if approximately one-half of the quinoline yellow S has been destroyed, the color is *fugitive.* If, when one-half of the color to be tested is destroyed, one-half of the color of congo orange R or alkali blue 6 B has disappeared, the color is *moderately fast;* if one-half of chrysamine G or naphthol blue black, it is *fast.* Finally, if when one-half of chrysamine G or naphthol blue black is destroyed, the color is hardly affected, it may be considered as *very fast* to light.

The terms applied to the fastness of colors to light are defined as follows: —

Very Fugitive. — The colors fade almost completely after exposure for 3 weeks to the sun in summer.

Examples. — Naphthol yellow S, new methylene blue N, and methylene green.

Fugitive. — They fade markedly in 6 weeks, and entirely at the end of a year.

Moderately Fast. — They fade distinctly in 6 weeks, and almost completely in a year.

Fast Colors. — They fade little in 9 weeks.

Very Fast. — After a year's exposure, a moderately good color remains.

Examples. — Alizarin cyanin R, and curcumin S.

Requirements for Fastness. — The fastness required of different goods varies according to the use to which they are to be put. The following are given as examples: —

Loose wool, slubbing, and weaving yarns must be dyed fast to light, milling, and potting.

Sewing cotton, carpet yarns, velvet, and plush must be dyed fast to light and rubbing.

Hosiery yarns require fastness to washing, perspiration, and rubbing.

Yarns for flannels, rugs, and blankets require a moderate fastness to milling, good fastness to perspiration and rubbing.

Cotton linings must be dyed fast to perspiration, rubbing, and calendering.

Shirt goods must be fast to light, rubbing washing, and perspiration.

Gentlemen's suitings must be fast to light and potting. The color must not rub off, and the goods must be well dyed through. The colors of military cloth should be particularly fast to light.

Ladies' dress goods must be fast to light, rubbing, and alkaline street dust.

Defects in Dyeing. — The defects in dyeing to which each class of colors is liable are given under the description of that class. We will here consider only some causes of defects not peculiar to any class of dye.

In cotton dyeing, *unripe cotton fibers* cause white specks; *motes* and *oil spots* lead to defects. Other defects may be traced to *faults in bleaching*.

In wool dyeing, *kemps* lead to defects in dyeing. Irregular dyeing may be caused by *injudicious blending* of different qualities of wool, which have different degrees of affinity for the dye; by *irregular weaving;* by the use of *yarns not uniform* in size, or twisted in different directions, or twisted with different tensions. *Imperfect scouring* of raw wool, by which wool grease is left on the fiber, will lead to defective dyeing. After scouring, wool should be thoroughly washed, as the *presence of alkaline bodies* (soap or sodium carbonate) may cause trouble. *Lime* in pulled wool must be removed before dyeing; the wool is treated with hydrochloric acid, washed thoroughly, and scoured. Dark spots may be caused by the *sulphur in wool;* if it comes in contact with iron, copper, tin, or lead while in the alkaline condition, as in scouring, the sulphides of these metals may be formed, and produce dark spots.

Bleeding or rubbing is sometimes due to *insufficient washing* of the cotton or wool after mordanting, or after dyeing; in the case of wool, especially when dyeing with direct cotton colors and mordant colors, these defects may also be caused by not boiling the wool with the dye for a sufficiently long time. On the other hand, *overboiling* may injure some colors, such as logwood, which are applied on a potassium bichromate mordant, on account of over-oxidation of the color. *Carbonized* wool, which has been insufficiently washed, is liable to be dyed unevenly.

The presence of certain *metals* must be avoided in particular mordant or dye baths. Copper affects the shade of some dyes injuriously, and so does iron, and their presence must be avoided in such cases. The effect of iron in a dye or mordant bath may be counteracted by placing a block of zinc in the bath; with this precaution, even iron vessels may be used.

Soaping. — Dyeing with certain colors, especially on cotton, is followed by working in a warm soap bath, or *soaping*. Soaping has the following objects: —

(1) It gives the material a softer feeling, and brightens the color.

(2) It removes loosely adhering particles of dye, and so prevents *rubbing*.

(3) It neutralizes any traces of mineral acid, and prevents *tendering* of cotton (a fatty acid is formed, which does not injure the fabric).

A careful soaping, after the production of some colors, is absolutely essential if freedom from rubbing is desired.

Silk Dyeing. — Silk dyeing is always carried out with the addition to the dye-bath of soap, or preferably *boiled-off liquor*, the alkaline liquor which results from the scouring and boiling off of raw silk with soap.

The boiled-off liquor acts in two ways: it preserves the luster and peculiar crisp feel of silk (known as the *scroop* feel), and it retards the combination of dyestuff with the silk fiber, thus aiding in the production of level shades.

The silk gum in solution combines with the dyestuff, first, and afterward the dyestuff is taken up more slowly by the fiber. The amount of boiled-off liquor to be employed depends upon the nature of the coloring matter employed; as a rule, it is about one-fourth to one-third of the total volume of the dye liquor. In silk dyeing, the dye-bath is seldom heated to a boil.

After the dyeing operation, silk is always "brightened," which gives it the scroop feel. It is passed through water slightly acidified with acetic, sulphuric, or tartaric acid, and rinsed without washing. The choice of acid depends to some extent upon the nature of the dyes employed.

CHAPTER XV

DIRECT COTTON COLORS

THE direct cotton colors are salts of color acids, and are direct dyes for all fibers. Since the first member of the group, congo, was discovered in 1884, great numbers of direct cotton colors have been placed on the market. The number is daily increasing.

Properties. — All the direct cotton colors are soluble in water, with the exception of some sulphur colors, which are soluble in sodium sulphide. They vary somewhat in solubility.

Like congo, they are decomposed by acids, the color acid being set free, as represented by the equation below: —

$$\mathrm{NaAc} + \mathrm{HCl} = \mathrm{NaCl} + \mathrm{HAc},$$

in which HAc represents the color acid. If the acid is a different color from the salt, the dye is not fast to acids. (How does acetic acid affect congo?)

Hard water precipitates most of the direct cotton colors in the form of calcium or magnesium salts. It should be softened before use in a dye-bath (see Exp. 5).

Some of the direct cotton colors also form insoluble salts with copper or chromium, which are less easily affected by light or washing than the corresponding sodium salts. Use is made of this property in the after-treatment of certain dyes, to increase their fastness. In other cases, the presence of copper in the dye-vat must be avoided, on account of its effect on the color.

Some direct cotton colors (such as primuline) can be diazotized and developed with the production of a color possessing a high degree of fastness to washing.

Application to Cotton. — The direct cotton colors are extensively used for dyeing cotton. On loose cotton, they have the advantage of leaving the cotton soft and in good condition for spinning. On yarn in cops, they are used on account of their easily leveling properties. On other classes of materials, the simplicity of the methods for applying them is a great advantage.

Methods of Dyeing. — The four chief methods of dyeing, differing, however, only in regard to the assistants added to the dye-bath, are as follows: —

(1) *Dyeing with Glauber's Salt or Common Salt and Soda.* — This may be regarded as the usual method, being employed with the majority of the dyestuffs, and for almost all shades. If it is necessary to retard the absorption of the dye, — as may be the case of pale tints, or thick materials which are difficult to dye through, — it is best to dye first for half an hour with soda, then add the Glauber's salt.

(2) *Dyeing with Glauber's Salt or Sodium Chloride Alone.* — This is used for dyes which cannot be dyed in the presence of soda; also for dyestuffs which are slowly removed from the dye-bath.

(3) *Dyeing with Glauber's Salt or Common Salt and Soap.* — This method is to be employed in all cases where slow dyeing is necessary, especially in the production of

delicate tints, or compound shades which are not easily matched, or with materials which cannot be properly dyed through by any other means.

(4) *Dyeing with Salts and Caustic Soda.*—The dyestuff is dissolved in caustic soda, and the solution added to the bath. Some dyes of this class require an after-treatment with sulphuric acid.

Other methods are used in particular cases.

The quantity of assistants to be used depends upon the nature of the dye and the depth of the color,—for light colors, one-half, and for delicate tints even one-fourth, of the quantity used for medium and dark shades.

The general method of dyeing is as follows:—

If soap, soda, or sodium phosphate is used, hard water may be softened by boiling it after the addition of any of these assistants. The bath is then prepared with the requisite ingredients, the color solution is added at once, and the material is entered at or near the boiling-point, and dyed at these temperatures 30 to 60 minutes. The goods may be dried without washing. In the case of goods sensitive to acids, their fastness is increased by a passage through a 5 per cent solution of sodium carbonate before drying.

Cold Dyeing.—Some of the direct cotton colors may be applied in a *cold* dye-bath.

EXPERIMENT 58.—Prepare a dye-bath with 2 per cent benzopurpurin 4 B and 20 per cent sodium chloride in 200 cc. water; enter a 10-gram skein of cotton yarn, heat to boiling, and boil half an hour, or until the skein is uniformly colored. Wash after dyeing.

Dye as above with 2 per cent diamine scarlet B, 50 per cent Glauber's salt, and 10 per cent soap.

Dye with 2 per cent chrysamine G and 20 per cent salt.

Dye with 2 per cent chrysophenin G and 20 per cent salt.

Dye with 2 per cent diamine blue 3 B, 20 per cent salt, and 3 per cent soda.

Dye with 2 per cent Chicago blue 4 R and 20 per cent salt.

Dye with 2 per cent congo orange R and 10 per cent salt.

Dye with 2 per cent toluylene orange G and 10 per cent Glauber's salt.

Dye with 2 per cent catechu brown and 10 per cent salt.

Dye with 2 per cent chromanil brown G and 10 per cent salt.

Dye with 2 per cent diamine violet N, 20 per cent Glauber's salt, and 3 per cent sodium carbonate.

Dye with 3 per cent oxamine violet and 5 per cent salt.

Dye with 2 per cent brilliant benzo green and 10 per cent salt.

Dye with 5 per cent pluto black G and 10 per cent salt.

Dye with 5 per cent diamine black BH and 10 per cent salt.

Dye with 5 per cent diamine black HW and 10 per cent salt.

What is the difference between the three blacks? Test fastness of all dyeings to acids, alkalies, and washing.

Assistants. — The dyeing of cotton with direct cotton colors always takes place in the presence of assistants, which are the neutral salts, Glauber's salt (sodium sulphate) and common salt (sodium chloride), and the alkaline substances, soap, soda, and sodium phosphate. The presence of alkaline substances (sodium carbonate, soap) retards the absorption of the coloring matter by the fiber, whereas the neutral salts (Glauber's salt, common salt) have the opposite effect; and the more salt the bath contains, the quicker the absorption takes place. Of course, undue excess of salt tends to precipitate the coloring matters, or to give irregular shades.

If added in considerable quantities, the salts raise the boiling-point of the dye-bath; and the increase in temperature thus obtained, though small, is of importance with some dyestuffs.

Glauber's salt is prepared by the action of sulphuric acid upon common salt. It occurs in two forms, — as crystals containing 55.9 per cent water, of the formula $Na_2SO_4 + 10\ H_2O$, and as the desiccated or anhydrous salt. 100 parts of desiccated Glauber salt are equivalent to 220 of the crystallized salt. Glauber's salt is sometimes adulterated with common salt.

Common salt, or sodium chloride $NaCl$, is found as rock-salt and in sea-water. It contains no water of crystallization. Common salt and Glauber's salt have the same action in dyeing with direct cotton colors, though Glauber's salt often gives the better results.

Sodium phosphate, or phosphate of soda, is found as crystals of the formula $Na_2HPO_4 + 12\ H_2O$. Its high price prevents it from being used in dyeing to any extent.

Sodium carbonate occurs as crystals, $Na_2CO_3 + 10\ H_2O$, containing 62.9 per cent water, known as soda crystals; as crystals carbonate, $Na_2CO_3 + H_2O$, containing 18 per cent water; and as water-free sodium carbonate, known as soda or "soda ash." Soda ash comes into the market in various strengths, chiefly 48°, 52° to 56°, and 58°, each degree indicating 1 per cent sodium oxide (Na_2O). Soda ash 58° contains over 58 per cent Na_2O, or from 98 to 99 per cent sodium carbonate, and is pure enough for all dyeing operations. The other brands contain chiefly harmless impurities, as sodium sulphate and sodium chloride; also some caustic soda, which is objectionable for some applications, while it is an advantage for others.

Production of Level Colors. — Direct cotton colors produce level dyeings on cotton with no particular precautions. The general rules for the production of a level color (Chapter XIV) apply here.

Cop Dyeing. — The dyeing is conducted at about 60° C., and the Glauber's salt is added after working five or ten minutes. In producing compound shades, it is best to dissolve each color separately, add about $\frac{2}{3}$ to the dye-bath, and the remainder gradually until the desired shade is produced.

Warps. — It is best to dissolve dyes and assistants separately, add $\frac{1}{10}$ to the dye-bath, and the remainder during the passage of the warp.

Cloth. — On the jigger and the padding machine, the same method may be pursued as for warps.

Mixing Direct Cotton Colors. — The direct cotton colors may be mixed unreservedly with each other in the same bath, so that almost any shade can be obtained by employing them in suitable combinations. In selecting dyes to be mixed, care must be taken to choose those which behave similarly both as regards absorption by the fiber and exhaustion of the bath. So far as is possible, it is best to select dyestuffs which require the same salts, alkalies, etc., in the bath. If this cannot be done, the addition of assistants is regulated by the dyestuff present in largest proportion.

Exhaustion of the Bath. — Cotton rarely removes direct cotton colors completely from the bath. The quantity left in the bath depends on: —

(1) *Volume of water used* being greater as the quantity of water increases.

(2) *The quantity of salts used* being less with increase in quantity of neutral salts.

(3) *The Affinity of Dye for Fiber.* — In this respect there is great variation. Some few of the group exhaust completely even when dyeing deep shades.

Except in the production of very light shades, which must be dyed slowly, and for which the exhaustion of the bath is of no consequence, the quantity of water in the bath should be reduced as much as possible. As a general rule, from 20 to 25 gal. of water should be used per 10 lb. goods to be dyed. Strong baths not only exhaust better, but produce deeper and fuller shades.

The exhaustion of the bath may be facilitated: —

(1) By working with a closed steam coil (the bath is not diluted with condensed steam).

(2) By increasing the quantity of salts used.

(3) By allowing the goods to cool in the bath for half an hour or longer, when "feeding" occurs.

Standing Baths. — When light shades are dyed with the direct cotton colors, the bath is often thrown away. With dark shades, however, one-third to one-fourth of the dye remains in the bath, as well as a large quantity of salts, and it is economical to use the same bath over and over again. Standing baths require the addition of water, to replace the loss by evaporation, or that carried away in the goods, salts, and dye to replace that taken off in the dyed material.

The quantity of *salts* in the bath may be controlled by the use of a delicate hydrometer. The density of the dyebath is determined before and after dyeing, care being taken that both determinations are made at the same temperature. Sufficient salts are then added to bring the bath to its former density.

In dyeing with a mixture of such colors as are not equally absorbed by the fiber, a little more of one than of the other is left in the bath. For a standing bath, a method of estimating and utilizing the color is to enter the next lot of goods without further addition of dyes. After allowing the residual color to be fully absorbed by the material, the shade thus obtained is examined, and from its appearance the practised eye can tell in what proportions the several colors should now be added in order to match the required shade.

After-treatment of Direct Cotton Colors. — Three methods of after-treatment for the purpose of increasing the fastness of direct cotton colors to light or washing are in use: —

(1) Diazotizing and developing.
(2) Coupling.
(3) Treatment with metallic salts.

Diazotizing and Developing. — The process consists of three steps: dyeing, diazotizing, and developing. For the chemistry of this process see p. 16. The dyeing is conducted in the usual way. After rinsing, diazotizing takes place in a bath made up with sulphuric or hydrochloric acid and sodium nitrite. The following precautions are usually necessary in diazotizing: —

(1) The bath should be kept cold, with ice if necessary.

(2) Development should take place as soon as possible after diazotizing, and the diazotized material should not be exposed to direct sunlight, or kept in a warm place.

The diazotizing bath is used continuously, being freshened up with about $\frac{1}{3}$ the quantity used for the first bath.

Control of the Diazotizing Bath. — The strength of the diazotizing bath may be exactly controlled by the following method: —

Dissolve 3.3 g. potassium permanganate in a liter of water. Measure off 25 cc. of the diazotizing bath with a pipette, dilute to 200 cc., add a few drops of sulphuric acid, and then, from a burette, permanganate solution until the liquid assumes a faint pink color. After diazotizing, this operation is repeated, and sufficient nitrite and acid is added to the bath to bring it to its former strength. For example; if 45 cc. of permanganate solution is required before, and 30 after, diazotizing, the addition of $\frac{1}{3}$ the quantity of nitrite and acid first used will restore the bath to its former strength.

Developing. — After diazotizing, the goods are entered into a bath of the proper developer, worked about 15 minutes, rinsed, soaped if necessary, and dried.

The various developing baths are for the most part unstable when exposed to the air. The best method of operation is to prepare a strong solution ("stock solution") of the required developer, and add it to the bath as may be required. Standing baths are freshened up by the addition of $\frac{3}{4}$ the quantity of developer used the first time.

The developer usually used is beta-naphthol. Other developers in use are naphthylamine-ether (amido-naphthol ether), toluylene diamine, resorcin, phenol, alpha-naphthol, and Schaeffer's salt. These developers are sold in various forms, as pastes, or powder, for example. They are also sold under different names, as blue developer, fast blue developer, etc. A few dyes are developed with a hot solution of soda. (See also p. 19.)

EXPERIMENT 59. — (1) Dye a 10-gram skein of cotton yarn with 1 per cent diaminogene blue G, 20 per cent Glauber's salt, and 2 per cent soda. Wash and remove a sample. Prepare a *diazotizing* bath with 1½ per cent sodium nitrite in 200 cc. water, to which 5 per cent hydrochloric acid is added, just before the skein is entered. Work cold 15 minutes, squeeze, and enter immediately in the developing bath of 0.3 per cent beta-naphthol[1] in 200 cc. water. Work cold 15 minutes, wash and dry.

(2) Dye with 6 per cent diazo black BHN, 20 per cent salt, and 5 per cent soda. Save sample. Diazotize and develop as directed above, using 2½ per cent sodium nitrite, 8 per cent hydrochloric acid, and 1 per cent beta-naphthol.

(3) Dye with 5 per cent cotton brown A and 20 per cent Glauber's salt. Save sample. Diazotize and develop, using 2½ per cent sodium nitrite, 8 per cent hydrochloric acid, and 1 per cent beta-naphthol.

Test fastness of colors to washing (Exp. 7) and boiling water (Exp. 6) before and after diazotizing and developing.

Experiment 13 also illustrates the method of diazotizing and developing.

Application. — Diazotizing and developing are used for the production of red, blues, and black, with a high degree of fastness to washing.

Loose cotton in nets may be placed in a vat containing the diazotizing liquid, lifted and allowed to drain, and placed in a rinsing vat, thence in the developer.

Warps require a warp machine with three compartments,

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[1] The beta-naphthol is dissolved with an equal weight of caustic soda.

each with its squeeze rollers. The best process is to prepare separate solutions of sodium nitrite and hydrochloric acid, add one-tenth to the diazotizing vat, and the remainder during the passage of the warp. The developer is added in the same way. The middle vat contains a rinsing liquor.

Cloth is treated in a similar machine.

Shading Developed Dyeings. — For obtaining the desired color with diazotized and developed dyes, the following methods may be employed: —

(a) *Simultaneous Dyeing with Several Diazotizable Colors.*

(b) *By employing Mixtures of Various Developers.* — Useful mixtures of this kind are: beta-naphthol and resorcin; beta-naphthol and phenylenediamine; phenylenediamine and resorcin.

Such developers as are applied in an acid bath cannot be mixed with such as are used in an alkaline bath.

(c) *Simultaneous Dyeing with Diazotizable and Non-diazotizable Colors.* — In this case, the non-diazotizable color must not be affected in shade to any extent by the diazotizing process. The color which is unaffected by the diazotizing process is, however, not fast to washing, and is liable to bleed.

(d) *Topping with Basic Colors.* — Like all other direct cotton colors, these colors can be combined with basic colors.

Coupling. — The chemistry of coupling is the same as the chemistry of diazotizing and developing. In coupling, the diazonium compound is formed in solution instead of on the fiber, and then is combined with the dye. Paranitraniline is the only substance used in coupling. A cold solution of paranitraniline in hydrochloric acid is treated with sodium nitrite, and sodium acetate to neutralize excess of hydrochloric acid is added, and the dyed fabric is passed through the solution, as in diazotizing. The color will *rub* if all the hydrochloric acid is not neutralized. The solution can be tested with a paper colored with congo red, which is turned blue if any free hydrochloric acid is present.

For details of the process see paranitraniline red (Chapter XIX).

Experiment 60. — Dye a 10-gram cotton skein (boiled off) with 5 per cent cotton brown A, 2 per cent soda, and 20 per cent Glauber's salt in 200 cc. water, boiling half an hour. Remove a sample. Mix 2 per cent paranitraniline mixture[1] with 100 cc. water, and add 1.3 per cent sodium nitrite. Stir well. When all is dissolved, add 4 per cent sodium acetate, and work the yarn in the solution 20 minutes. Rinse and dry.

After-treatment with Metallic Salts. — This increases fastness to light and washing. The salts used are copper sulphate, potassium bichromate, and chromium fluoride. With copper sulphate or chromium fluoride, copper or chromium salts of the color acid are probably formed, which are affected by light to a less extent than the sodium salt, and, being less soluble in water, do not bleed or wash out so readily. With bichromate of potash, the action is probably different; the color acid is oxidized to some

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[1] Paranitraniline mixture. Heat 10 g. paranitraniline and 16 g. hydrochloric acid (1.20 sp. gr.) in 400 cc. water until dissolved, and add 1800 cc. cold water. 20 cc. = 0.1 g. paranitraniline.

extent, and also converted into the corresponding chromium salt.

As many direct cotton colors are altered considerably in shade by the after-treatment, it is necessary, in order to be sure of the ultimate result, to make laboratory dye-trials to determine what these alterations are, and make proper arrangements for producing the desired shade. For *shading*, dyes must be used which are not changed by metallic salts.

Application. — The dyed fabric is treated with a solution of the salts at the proper temperature, washed and dried. In *warp* dyeing, the salts are best added in portions during the passage of the warp.

Experiment 61. — (*a*) Dye cotton yarn with 5 per cent diamine jet-black CR, 1 per cent soda, and 10 per cent Glauber's salt in 200 cc. water, boiling half an hour. Wash, remove sample, and boil remainder 15 minutes with 4 per cent potassium bichromate in 200 cc. water.

(*b*) Dye with 2 per cent Chicago blue 4 B, ½ per cent soda, and 5 per cent Glauber's salt. Wash, remove sample, and boil remainder as above with 3 per cent copper sulphate in 200 cc. water.

(*c*) Dye with 4 per cent benzo-chrome brown G and 5 per cent salt; wash, remove sample, and boil remainder 15 minutes with 3 per cent copper sulphate, 3 per cent potassium bichromate, and 2 per cent acetic acid in 200 cc. water.

Test fastness of dyeings to washing and to boiling water, before and after treating with metallic salts. Does the treatment affect the color of the yarn?

Defects in Dyeing. — Defects in dyeing direct cotton colors may be traced to insufficient preparation, or faulty manipulation. Spots, streaks, or stains may be due to oil spots, faulty wetting-out, defects in bleaching, or to not boiling for a sufficient length of time in the dye bath. Direct cotton colors, as a rule, yield good dyeings very easily.

Sulphur Colors. — The sulphur colors are a group of direct-dyeing cotton colors (mostly black and brown) made by fusing various organic bodies with sulphur and alkalies. They are characterized by a high degree of fastness to light and washing, and are becoming of great importance.

Properties. — The sulphur colors are, as a rule, insoluble in water, and are dissolved with the aid of sodium sulphide. The dye probably exists in a reduced form in the bath, and is afterward oxidized on the fiber. The oxidation often takes place on the surface of the liquid with the formation of a scum. Most sulphur colors are precipitated from solution by copper, so that copper cannot be used in dye-vats. Iron or lead pipes and iron or wooden rollers are used. Most sulphur colors require an after-treatment to develop the color.

The tinctorial power of these dyes is low, as they require from 10 to 50 per cent to produce full shades. They have recently been prepared in more concentrated forms, 4 to 5 per cent producing a full black.

Sulphur colors are used mainly on cotton. The dyes have no great affinity for the fiber, and standing baths should be used.

Sulphur colors are oxidized and injured if exposed to the air. They must be kept dry, and in well-closed vessels.

Sodium sulphide occurs in two forms: as the crystallized salts, and as the fused salt, the latter being about twice as strong as the former.

Methods of Dyeing. — The dye should be dissolved very carefully in hot water, with the addition of sodium sulphide if necessary. The bath is prepared with the necessary salts and the color solution added, and the dyeing conducted at or near the boil. As a rule, the bath should be kept as a standing bath, since large quantities of the color usually remain in it. The sodium sulphide is gradually oxidized by the air; a sufficient quantity of it should be used to keep the bath free from particles of undissolved dye. If too little sodium sulphide is present, the liquid is turbid, and particles of dye are seen if liquor is dropped on blotting paper. If too much is present, the dyeing lacks depth.

Certain sulphur colors require hardly more precaution in dyeing than ordinary direct cotton colors. Others require careful protection of the goods from the air, to prevent superficial oxidation of the color. However dyed, the goods must be squeezed free of the excess of dye liquor as soon as they are removed from the bath, and carefully rinsed; otherwise the color contained in the dye liquor will be oxidized and fixed superficially, with the result that the dyeing will rub.

Machines or vats for dyeing with most sulphur colors must not contain brass or copper. *Skeins* are hung on bent iron rods , so that they are completely immersed in the bath, and can be turned without being lifted above the surface of the liquid. *Warps* are dyed in the usual form of machine, provided with iron or wooden guide rollers which are completely immersed in the liquid. *Cloth* is dyed on the jigger, or the hawking machine; it must pass between squeeze rollers, and be washed as soon as it leaves the dye-vat.

After-treatment. — Most sulphur colors require an after-treatment. The methods used are: —

(*a*) Oxidation by

(1) Potassium bichromate;
(2) Hydrogen peroxide;
(3) Steaming and exposure to the air.

(*b*) Treatment with copper sulphate.

The methods are illustrated by the following experiment.

EXPERIMENT 62. — Dye three 10-gram skeins of cotton yarn (wetted-out) as follows: —

(1) Mix 2 g. sulphur-black T with 2.5 per cent caustic soda and 4 g. sodium sulphide in 60 cc. water, and boil until dissolved. Dilute to 200 cc., and add 1 per cent soda and 10 g. Glauber's salt. Boil the yarn in this solution for 30 minutes. Wash well and dry. Save the bath.

(2) Mix 2 g. immedial blue C with 8 per cent soda and 8 per cent sodium sulphide in 100 cc. water. Boil until dissolved, dilute to 200 cc., and add 5 g. salt. Enter the skein and boil 30 minutes. Save the bath. This dye requires an after-treatment. Rinse the skein and develop the color in a cold bath of 10 cc. hydrogen peroxide[1] and 10 cc. ammonia in 200 cc., working 10 minutes.

(3) Mix 3 g. autogene black, 7 per cent salt, and ½ per cent sodium carbonate with 200 cc. water, heat until dissolved. Enter the yarn and boil 30 minutes. Remove and wash. Save the bath.

Test fastness of all three skeins to washing and to boiling water. Place 2 or 3 g. of copper in each dye-bath, after it has been used, and boil 15 minutes. Examine bath and copper. What effect has the copper?

Soaping. — A soaping, after completing the dyeing with sulphur colors, has two objects: —

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[1] Hydrogen peroxide, 1½ volumes commercial diluted to 10. Ammonia 1½ volumes diluted to 100.

(1) It neutralizes mineral acids which have not been completely washed out.

(2) It softens the goods, and removes loosely adherent dye.

Defects in Dyeing. — For perfect dyeing with sulphur colors, the following are essential: —

(1) *Careful Solution.* — The dye liquor should be clear, and kept clear by the addition of sodium sulphide if necessary.

(2) *Squeezing* immediately after removal from dye-bath, to press the liquor out uniformly. It has a tendency to collect at the edges of cloth.

(3) *Careful rinsing*, immediately after dyeing, to remove the excess of dye liquor; and after after-treatment, to remove all traces of acids.

If not properly applied, sulphur colors may tender the goods, or be defective in appearance.

Tendering. — Tendering may be traced to insufficient washing of the goods, or to exposure to the air while dyeing. Any sodium sulphide left on the material will be gradually oxidized, and under some circumstances, as exposure to the air, free sulphur is precipitated on the goods, which is gradually oxidized to sulphuric acid. Tendering may be prevented by the addition of sodium acetate to the last wash water; it will neutralize the mineral acid, with the formation of acetic acid, which will not injure the goods.

Tendering may also be traced to over-oxidation during the after-treatment with potassium bichromate, or insufficient removal of the mineral acid used in the after-treatment.

Bronzy appearance of goods dyed with sulphur colors is due to improper manipulation in the dye-bath, with exposure to air during dyeing. *Rubbing off* of the color is due to the same cause.

Topping Direct Cotton Colors with Basic Colors. — The direct cotton colors, whether after-treated or not, have the power of combining with basic colors. This property is utilized for shading direct cotton colors, as well as, to some extent, for dyeing basic colors. It will be discussed in detail under that head. Sulphur colors may be topped with basic colors, with the production of quite fast dyeings.

Fastness of Direct Cotton Colors. — The direct cotton colors, with the exception of the sulphur colors, bleed into white cotton, unless they are after-treated, even though they often lose little color in washing. Some of them are sensitive to acids, particularly the reds. When properly dyed, rubbing off is out of question. Dyeings diazotized and developed or after-treated, are very fast to washing.

Application to Linen. — Direct cotton colors do not possess the requisite degree of fastness for application to linen. After-treatment renders them sufficiently fast. The methods are the same as for cotton. Sulphur colors are used to a considerable extent on linen.

Application to Wool. — The direct cotton colors are not employed to a large extent for wool, as the acid dyes are much cheaper. Some of them possess an excellent fastness to milling. They are used largely in dyeing union goods (cotton and wool).

They are applied to wool in neutral baths, with or without the addition of common salt or Glauber's salt. In some cases, wool is dyed with these colors in a bath acidified with acetic acid, and, if necessary, the color is then developed in a weak solution of soda.

Application to Silk. — Some of the direct cotton colors are of excellent fastness to water, washing, and milling on silk.

The colors are applied in a soap-bath acidified with acetic acid. Enter at 45 to 60° C., bring almost to a boil, and after handling three-quarters of an hour, add 2 to 4 per cent acetic acid, and exhaust the bath slowly. Rinse and brighten.

After-treatment. — When great fastness is required, these dyes may be after-treated on silk with metallic salts or by diazotizing and developing. The methods used are practically the same as for cotton. An excessive amount of metallic salts may cause damage.

After developing, the silk is passed through sulphuric acid to brighten. To produce the best results, the silk should be soaped in a boiling hot soap-bath after developing, then rinsed and brightened.

CHAPTER XVI

BASIC COLORS

THE basic colors are salts of organic color bases, and, as we have seen in the case of fuchsine, they are direct colors for wool and silk, but dye cotton only with the aid of a mordant. The basic colors are the oldest artificial colors known. The first number of the group, discovered in 1856, was the first artificial dye manufactured.

Composition. — The basic colors are generally sold in the form of their hydrochloric acid salts, but some are brought into commerce as acetates, oxalates, sulphates, nitrates, or as double salts of hydrochloric acid and zinc chloride; in rare cases in the form of the free color base. They are sold as pastes, powders, or crystals, the latter being the most concentrated form. In some cases the crystals are very nearly pure, while as a rule the powders or pastes are purified to a less extent.

Properties. — Most of the basic colors are soluble in water, while all dissolve in alcohol. Generally they require about 250 times their weight of hot water for solution. A few, such as auramine, are decomposed by hot water.

Hard water with temporary hardness acts upon these dyes by throwing down the color base in the form of a curdy precipitate, thereby rendering a part of it useless for dyeing purposes; while further injury may be caused by the precipitate being deposited on the goods, giving rise to spots and unevenness, *dye-spots*.

Hard water may be corrected by the addition of sufficient sulphuric or acetic acid to decompose the carbonates (see Chapter XIII).

The basic dyes possess great tinctorial power, and produce full shades with very small amounts of dye. They are characterized by their brilliancy and purity of hue.

Application to Cotton. — Basic colors are dyed on cotton by several methods: —

(1) *Direct Dyeing.* — A few basic dyes are used for producing delicate tints on bleached cotton.

(2) *Tannin Mordant.* — The cotton is mordanted with tannic acid, which is fixed by means of salts of antimony or iron, and then dyed.

(3) *Aluminium Mordant.* — Aluminium hydroxide acts as the mordant. This is rarely used.

(4) *Dyes as Mordants.* — Direct cotton colors here serve as mordants for the basic dyes. This process is assuming greater importance every year.

(5) *Turkey-red Oil Mordant.*

Tannic Acid. — Tannic acid is used as a mordant for basic colors in several forms: —

(1) As sumac, or gallnuts.

(2) As extracts, more or less purified, of gallnuts, sumac, or myrabolans.

(3) As purified tannic acid.

Sumac consists of the leaves and twigs of several species of Rhus. It is sold in the form of the whole or crushed leaves, or as a powder; the leaf-stalks and small twigs are often admixed. The value of sumac depends upon its content of tannic acid, which may vary considerably. Best sumac contains 15 to 20 per cent tannin, and has an olive-green color, and a fresh, agreeable odor. Sumac dull in color and odor has been deteriorated by moisture and long keeping. Sumac contains some reddish coloring matter, which is taken up by cotton along with the tannic acid. Hence it cannot be employed in the dyeing of light and brilliant shades. Purchases of sumac should be based upon a guaranteed content of tannic acid and low amount of coloring matter.

Gallnuts are the excrescences on oak trees, caused by certain insects. The best gallnuts contain 55 to 60 per cent tannic acid. Chinese and Japanese gallnuts (from Rhus) may contain 65 to 70 per cent.

Myrabolans are the fruit of several kinds of trees growing in China and the East Indies. They contain much coloring matter.

Chestnut extract is a dark-colored extract from chestnut, and is used in the black dyeing, and weighting of silk.

Extracts. — Ordinary sumac extract occurs as a thick, dark-brown liquid, containing the tannic acid and coloring matter of the sumac. In the *decolorized* extract, the coloring matters have been removed. Decolorized extract can be used even for light shades. Purchases should be based upon actual content of tannic acid. Myrabolans extract is similar to sumac. Gallnut extract is purer, and compares with the decolorized sumac extracts.

Tannic acid, $C_{14}H_{10}O_9 + 2\,H_2O$, is prepared from *gallnuts.* The gallnuts are extracted with water or a mixture of water, alcohol, and ether, the aqueous solution separated, evaporated, and purified. Tannic acid occurs as (*a*) a colorless amorphous mass, (*b*) light yellow to buff-colored scales, (*c*) brittle vitreous masses. It is soluble in 6 parts of cold water, and more readily in hot water. Its solubility is decreased by sulphuric or hydrochloric acid, sodium chloride, and some other salts, and it can be precipitated (salted out) from strong aqueous solution by these substances.

A solution of tannic acid in water decomposes gradually on standing. An addition of borax hinders this change. It is easily oxidized and acts as a reducing agent. Its alkaline solution rapidly absorbs oxygen from the air, and becomes brown.

Salts. — Most of the salts of tannic acid are insoluble in water, but are easily soluble in acids. It is difficult to prepare them in the pure state.

Hard Water. — The quantity of tannic acid extracted from sumac by water decreases as the water grows in hardness, while the quantity of the non-tannin matters increases. In one instance with a very hard water, only 9 per cent of the tannic acid in the sumac was extracted. Hard water should not be used for preparing mordant baths with sumac.

Affinity for Cotton. — The affinity of cotton for tannic acid varies according to the conditions, as follows: —

(1) The more concentrated the solution, the greater the quantity of tannic acid absorbed by the cotton.

(2) The longer the cotton and solution remain in contact, the more tannic acid is absorbed. In six hours, nearly four times as much tannic acid was absorbed as in an hour.

(3) The lower the temperature of the solution, the greater the quantity absorbed. Cotton took up 17 times as much tannic acid from a cold solution as from a boiling one.

(4) The addition of salts causes more tannic acid to be taken up.

Under very favorable conditions, cotton absorbs only 30 per cent of the tannic acid in solution. Considerably less is usually taken up in practical work. As far as possible, a standing bath should be used for mordanting with tannic acid.

Antimony Salts. — The salts of antimony used in fixing tannic acid are as follows: —

Antimony potassium tartrate, or tartar emetic, $2\ K(SbO)C_4H_4O_6 + H_2O$, is the principal salt of antimony used in dyeing. It is not very soluble in water, and should contain 43 per cent Sb_2O_3.

Antimony sodium fluoride, $NaSbF_4$, is readily soluble in water, and 66 parts are equal to 100 parts tartar emetic.

Antimony salt (*Haen*), $SbF_3(NH_4)_2SO_4$, is a double salt of ammonium sulphate and antimony fluoride.

Double oxalate of antimony and potassium, $SbK_3(C_2O_4)_3$.

Mordanting with Tannic Acid. — Two methods are in use: —

(1) Loose cotton and yarn are entered in a hot or boiling bath containing the necessary quantity of tannic acid, worked well, and soaked for 3 to 12 hours, or over night, while the bath cools. The material is squeezed or hydro-extracted, washed lightly, and the tannic acid fixed as described below.

(2) For warps and piece goods a stronger solution of

tannic acid (2° to 3° Tw.) is used. They are run through the warm solution, squeezed, and fixed after they have stood some hours.

The strength of the tannin liquor to be used depends on the depth of the color desired. The baths are used continuously; exhaustion is aided by the addition of salt.

Fixing Tannic Acid. — Two methods of fixing are generally used, namely, with antimony and with iron.

Antimony. — The process is very simple. The mordanted cotton is passed into a bath of ½ to 3 per cent of tartar emetic, or corresponding amounts of other antimony salts, at 30° to 50° C. The baths are used continuously, their strength being restored from time to time, while the acid produced in the fixing process is carefully neutralized with soda, or chalk may be added to the bath for the same purpose. The cotton must be washed very carefully after fixing, as superficially fixed antimony will not only give rise to rubbing of the color, but may produce blood-poisoning if it comes in contact with the skin. For some colors a soaping before dyeing is necessary.

Iron. — Iron salts can be used only for dark shades. The fixing-bath is prepared with copperas (ferrous sulphate) or "nitrate" of iron, with the addition of some chalk to neutralize the acid which is liberated during the fixing process.

Dyeing. — The dyeing is conducted in a cold or warm bath, and the solution of the color is added in several portions to insure level dyeing. The time required is 30 to 60 minutes. Hard water is neutralized with acetic acid. If the color is apt to dye uneven, the addition of some acetic acid will cause it to go on the fiber more slowly and evenly. Undissolved particles of color will cause dye-spots. The bath should be exhausted.

EXPERIMENT 63. — In mordanting and dyeing, work carefully so that the mordant and dye will be taken up evenly. These dyes are not as easily applied as the direct cotton colors. See that your boiled-off skeins are thoroughly wetted out.

Mordanting. — Work 8 boiled-off skeins of cotton yarn in a *clear* solution of 5 g. tannic acid in 1000 cc. water for 15 minutes, and allow to stand half an hour, working occasionally. Squeeze. Fix the tannic acid by working 5 minutes in a bath of 2 g. tartar emetic in 1000 cc. water, and allow the skeins to remain in this bath 15 minutes, or until you are ready to dye them.

Dyeing. — Make up a bath of ½ per cent acetic acid and ½ per cent chrysoidine R in 200 cc. water; enter a skein and work carefully 5 minutes; raise the temperature to 50° and remove the flame. Allow the skein to remain in the bath half an hour, working from time to time. Wash.

Dye a second skein with ½ per cent methyl violet 5 B; a third with ½ per cent cresyl blue; a fourth with ½ per cent malachite green; a fifth with ½ per cent brilliant saffranine; a sixth with ½ per cent brown JE; a seventh with ½ per cent crystal violet; an eighth with ½ per cent auramine. Use in each case ½ per cent acetic acid, and follow directions above given. Test fastness of all skeins to washing.

Janus Colors. — The Janus colors may be applied like ordinary basic dyes. Another method is recommended: the material is dyed at a boil with salt and sulphuric acid, then fixed in a boiling bath of sulphuric acid, tartar emetic, and tannic acid.

After-treatment with Tannic Acid. — The fastness of the dyeings are increased by an after-treatment with tannic acid. After dyeing, the goods are passed through a bath of 2 per cent tannic acid, and rinsed thoroughly.

Mordanting with Turkey-red Oil or Soap. — This process gives very bright colors, but not at all fast. It is little used. The goods are soaked in a bath of Turkey-red oil or soap, dried and worked in a bath of aluminum acetate, washed and worked again in soap; finally washed and dyed as described above.

Alum Mordant. — This gives bright though fugitive shades. The goods are treated in a boiling bath of about $\frac{3}{4}$ oz. alum per gallon water, and then passed through a tepid bath of soda, wrung out, dried, and dyed. The soda precipitates aluminium hydroxide on the fiber, which acts as a weak acid.

Dyes as Mordants. — The use of basic colors to top other dyestuffs, especially direct cotton colors, is very important. The color base of most basic colors has the property of uniting with the color acid of direct cotton colors, forming insoluble compounds. The basic color is thus fixed fast to washing. The compound is, in many cases, decomposed if it is heated above 70°. Numerous compound shades may be produced by topping direct cotton colors with basic colors, and by combining basic colors with other dyes for which they have some affinity. They are used to brighten the color of alizarin, logwood, and aniline black.

The operation of topping is very simple. The material is worked in a cold or warm bath of the dye for about half an hour. It is then rinsed and dried.

Experiment 64. — Dye with 2 per cent thioflavin S as directed in Exp. 58, and top with $\frac{1}{2}$ per cent malachite green (Exp. 63). Test fastness to washing.

Fastness of the Colors. — The basic colors on cotton are not very fast to washing, though they do not bleed. They are, as a rule, not very fast to light.

Defects in Dyeing. — *Dye-spots* are caused by undissolved particles of the dye, or precipitation of the color base by hard water.

Rubbing is due to incomplete washing after mordanting and before dyeing.

Uneven dyeing is caused by uneven mordanting, or too rapid absorption of the dyestuff. Addition of acetic acid to the bath causes the dye to be absorbed less rapidly.

Stripping. — Basic colors may be stripped from the fiber by boiling with dilute sulphuric acid.

Basic Colors on Wool. — Wool does not have so great affinity for basic dyes as for acid dyes; consequently it is less difficult to produce level shades with basic dyes. The wool plays the part of an acid, combining with the color base to form a lake.

Dyeing. — Basic dyes are applied to wool in a neutral bath, or in a bath made slightly acid with acetic acid. Acetic acid prevents spotting due to precipitation of the free color base. An excess is to be avoided, as it retards the exhaustion of the bath. Basic dyes are sometimes dyed with the addition of soap, which increases the brilliancy of the shade. In dyeing with certain green dyes, the wool is mordanted with sulphur.

The dye should be dissolved in hot water, and added to the dye-bath through a cloth filter. If the water is not pure, its hardness should be corrected with acetic acid.

The two methods of dyeing are as follows: —

First Method. — The bath is made slightly acid, and the color solution added. If the color is apt to dye uneven, the wool is entered at a moderate temperature, otherwise it is entered into the boiling bath. After 15 to 30 minutes at or near the boil, the temperature is allowed to fall to from 60° to 70°, the wool is taken out and washed without much delay and dried.

Second Method. — The water is boiled well with 2 to 4 per cent soap, the sticky scum removed, and the color solution added. The dyeing proceeds as by the first method. The bath is not exhausted, and is used continuously.

Experiment 65. — Dissolve 1 per cent methyl violet 6 B in 200 cc. water, enter a 5-gram skein of wool and boil half an hour. Is the bath exhausted?

Dye skeins with 1 per cent methyl violet 4 R,
1 per cent malachite green,
1 per cent Bismarck brown,
1 per cent thionine blue,
1 per cent saffranine M,
1 per cent wool blue,
1 per cent auramine.

Test fastness to washing.

Sulphur Mordant. — Brighter and faster dyeings with malachite green and brilliant green are obtained on a sulphur mordant. The method is illustrated by the following experiment: —

Experiment 66. — Dissolve 20 per cent sodium thiosulphate, 10 per cent alum, and 4 per cent sulphuric acid in 200 cc. water. Enter a 5-gram skein of wool, heat to 75° C., and keep near this temperature for half an hour. The thiosulphate is decomposed, sulphur separates in a finely divided form, and is absorbed by the wool. Dye the mordanted skein and an unmordanted skein in the same bath with 2 per cent malachite green. Test fastness to washing.

Fastness of the Colors. — The following are the characteristic features of the colors produced on wool by means of the basic dyes: great brilliancy of shade, evenness of dye, good penetration, marked rubbing off, want of fastness to light, moderate fastness to washing, and a great tendency to bleed.

Defects. — *Dye-spots* are caused by precipitation of the color base in the dye-bath by hard water, or by imperfect solution of the dye.

Basic Colors on Silk. — Silk has a greater affinity for basic dyes than wool, and gives faster colors.

Silk is dyed in a neutral or alkaline bath, or one slightly acidified with acetic, tartaric, or sulphuric acid. Usually soap or boiled-off liquor is added to the dye-bath. The general process is as follows: —

The bath is made up with 1 to 2 per cent soap, or 10 to 30 per cent boiled-off liquor, then acetic acid is added until the alkaline reaction has almost or entirely disappeared, and finally the carefully dissolved dyestuff is added. The silk is entered at 30 to 40° C.; the temperature is raised to near the boil, while continually handling the material, the dyeing being completed at 80 to 90° C. The process is accelerated by raising the temperature and by having the dye-bath weakly alkaline; on the other hand, it is retarded if the bath is kept slightly acid.

The dyeing process may be regulated by varying the acidity of the bath. In the case of full, deep shades, the bath is kept as neutral as possible, in order to utilize the dyestuff to its fullest extent, since the large quantity of dye present will insure the even dyeing of the silk. With pale, delicate shades, it is customary to work with a slight excess of acetic acid in the bath, to prevent the fiber from taking up the color too rapidly, and to insure that it will be evenly dyed.

After dyeing, the silk is brightened.

After-treatment. — The fastness to washing of the basic colors on silk can be greatly improved by an after-treatment with tannic acid and tartar emetic.

The dyed silk is best kept over night at 48 to 60° in a tannin bath containing 1 per cent pure tannic acid, then fixed at 60° without rinsing in a bath of 8 oz. tartar emetic per 10 gal. water, rinsed, soaped, and brightened.

For less brilliant shades, sumac may be employed in place of tannic acid.

CHAPTER XVII

ACID COLORS

Acid colors possess a distinctly acid character, and are dyed on the animal fibers as the free color acid. With the exception of picric acid, the acid colors are sold as salts, mostly alkali salts, but a few in the form of lime salts.

Properties. — With few exceptions, the acid colors dissolve readily in hot water, requiring about 25 to 50 times their weight of water for solution. Hard water is not very injurious in dyeing wool with these colors, as the lime salt of the dye is decomposed by the acid added to the bath. However, it is best to use distilled water. The acid colors do not possess great tinctorial power. About 3 per cent of color is usually required for a full shade on wool.

Application to Cotton. — The dyeings with acid colors on cotton do not possess any fastness to water and washing. As they are not sensitive to acids, and some of them are faster to light than the direct cotton colors, they find a limited application on some classes of material which do not require to be washed.

Methods of Dyeing. — The dye-bath should be as concentrated as possible in order to produce full shades. It is never exhausted by the cotton, but is used continuously as far as possible.

The methods of dyeing acid colors on cotton are illustrated by Experiment 23, Chapter IV (which see).

They are usually applied with the alum mordant in the dye-bath.

Application to Jute. — Acid colors are dyed on jute with the addition of 2½ per cent oxalic acid or alum. For some colors, the basic alum mordant used for cotton may be used (Exp. 23).

Application to Wool. — The acid dyes are used to a great extent on wool, both on account of their cheapness and for the reason that they are easily applied.

The process of dyeing with acid colors on animal fibers is to be regarded as a salt or lake formation, in which the wool or silk acts the part of the base, while the color acid plays the part of the acid. The chemistry of the process has already been discussed.

Methods of Dyeing. — The exact method for applying the acid colors to wool depends upon the nature of the material and its form, and the affinity of the dye for the fiber.

Level-dyeing acid colors, or those which do not go on the fiber too rapidly, are applied as follows: —

The bath is prepared with the necessary quantity of dye, 10 per cent Glauber's salt, and 4 per cent sulphuric acid. The wool is introduced and worked continuously, while the temperature is raised to the boil. The dyeing is complete in 1 to 1½ hours. In place of Glauber's salt and sulphuric acid, 10 per cent bisulphate of soda may be used.

In some cases, as with very loose yarns and with dyes which level easily, the wool may be entered directly into the boiling bath.

For *ordinary acid dyestuffs*, or when the goods must not be allowed to take up the dye too rapidly (as in the case of warps, or heavy material), the following precautions are used : —

The material is introduced in the bath at a low temperature with a slight addition of acid, and the remainder of the acid is added in small portions to the boiling bath. The temperature must not be raised to the boil too rapidly.

Special methods must be used for some dyes. The following are examples : —

Dye with 10 to 20 per cent Glauber's salt and 5 per cent acetic acid. After boiling for some time, add 5 per cent sodium bisulphate, or 2 to 5 per cent sulphuric acid, which exhausts the bath.

Dye with Glauber's salt and acetic acid, and exhaust the bath by the addition of more acetic acid.

Dye with Glauber's salt and acetic acid alone.

Dye with ammonium acetate. The bath slowly becomes acid by the decomposition of this salt.

EXPERIMENT 67. — Prepare the bath with 1 per cent of the dye, 10 per cent Glauber's salt, and 4 per cent sulphuric acid. Enter the wool, heat to boiling, and boil 30 minutes. Observe if the bath is exhausted, and test fastness to washing.

Dye 5-gram skeins with each of the following colors : —

Skein No. 1. Fast red A extra.
2. Indian yellow.
3. Ponceau R.
4. Acid violet 4 RS.
5. Acid green BN.
6. Wool blue R (use 3 per cent acetic acid instead of 4 per cent sulphuric acid).
7. 5 per cent wool black 4 B.
8. Quinoline yellow.

Alkali Colors. — This is a special class of acid dyes, which must be applied in an alkaline bath, and the color developed afterward by treatment with an acid (see Exp. 24). The dye-bath is not exhausted.

Experiment 68. — Dye a wool skein with $\frac{1}{2}$ per cent Nicholson's blue 4 B and 4 per cent borax in 200 cc. water, boiling half an hour. Remove a sample. Develop in a warm bath (50° C.) of 2 per cent sulphuric acid in 200 cc. Explain the change in color. Test fastness to washing.

Level Dyeing. — Apart from imperfect preparation of the material, or faulty construction of the dye-vat, stripes, cloudiness, and imperfect penetration of acid dyes are caused by the absorption of the dyestuff by the wool too rapidly.

The following circumstances favor level dyeing: —

(1) Old dye liquors, *i.e.* baths which have been used several times for dyeing.

(2) An increased amount of Glauber's salt. The Glauber's salt retards the absorption of the coloring matter, and it exercises a solvent action on the particles already attached to the wool, taking the dye from the darker portions of the material, and thus affording the lighter portions an opportunity for taking up the excess. An increased amount of Glauber's salt is employed when dyeing pale shades, when dyeing thick, closely woven goods, and indeed whenever the dyeing appears irregular.

(3) Regulating the amount of acid, or using weaker acids. The acid acts chemically upon the fiber, and also liberates the free color acid of the dye, which unites with the wool the more rapidly the more completely it has been set at liberty. The acid may be regulated (1) by using a

smaller amount, (2) by using weaker acids, as acetic acid, (3) by adding the acid to the bath gradually and in small portions at a time.

(4) Regulating the temperature. The higher the temperature of the dye-bath, the more rapidly is the coloring matter taken up by the wool. Hence, by raising the temperature of the bath slowly, the rate of dyeing can be lowered. Some few dyes dye more level shades if the goods are entered at the boil.

Mixing. — Acid dyes may be mixed in every proportion. It is best to mix colors which require the same methods of application; otherwise the dyeing process must be that required by the least easily leveling color.

For *shading*, or *color matching*, the additions to the bath should always consist of easily leveling dyestuffs.

Exhaustion of Bath. — The acid dyes are always exhausted (or nearly so) from the bath by wool, with the exception of alkali blues, which are dyed in a standing bath where possible.

Defects in Dyeing. — The following irregularities may be met with in dyeing wool with acid dyes: —

(1) Dye spots, *i.e.* deeply dyed spots or specks on the goods.

(2) Irregular dyeing, as cloudiness, dark or light streaks, and pieces not dyed through, that is, the surface of the cloth is darker than the interior.

(3) Speckled goods.

(4) Rubbing off of the color.

Dye-spots are sometimes due to defective scouring and washing of the material. Dye-spots are liable to occur when the color acid of the dyestuff employed is sparingly soluble, or insoluble, especially if it tends to become resinous or tarry in the hot dye-bath, forming sticky globules which adhere to the wool.

In preventing dye-spots, the aim is to precipitate the color acid in as fine a state of division as possible, and through the whole bath, so that the particles remain separate, and gradually dissolve in the bath without combining to form globules.

Dye-spots may be prevented: —

By dissolving the dyestuff in boiling water, filtering, and pouring it gradually in the bath.

By adding the acid or bisulphate of soda to liberate the color acid after the goods have been boiled in the dye-bath with the dye for some time.

Dye-spots are sometimes formed when a new bath is charged with Glauber's salt, sulphuric acid, and dye at the ordinary temperature, by the bubbles of air expelled from the water when it is heated carrying particles of color acid to the surface, where they form a scum which produces dye-spots on the goods. If, after charging with sulphuric acid and Glauber's salt, the bath is heated to a boil, and the color solution then added, no scum is formed, since the gases have been expelled.

Irregular dyeing is due to too rapid combination of dye and fiber, and is to be prevented by taking the precautions already given for level dyeing.

Speckled Dyeing. — Some dyes have a greater affinity for one end of a wool fiber than for the other. This form of irregular dyeing gives a speckled appearance to the goods. The defect may be lessened somewhat by using the precautions for level dyeing, but in some cases the dye must be discarded.

Experiment 69. — Prepare a bath with 7 per cent nigrosine S.I.W. (soluble in water), 10 per cent Glauber's salt, and 1 per cent acetic acid. Enter a 5-gram skein of wool, boil 20 minutes, remove, and add 4 per cent acetic acid. Again enter the wool, and boil 20 minutes. Is the color uniform? Explain.

Rubbing. — Certain acid colors are prone to rub, if the dye-bath is not exhausted. For these colors, an excess of dyestuff in the bath must be avoided.

Fastness. — The acid dyes vary considerably in fastness. Some of them are very fast to light and washing, but many of them bleed in milling.

Acid Dyes on Silk. — Silk does not possess as great an affinity for acid dyes as does wool; many acid dyes are removed from silk even by washing with water.

Methods. — Silk is dyed in a bath of boiled-off liquor, or soap made acid (broken) with sulphuric acid. Boiled-off liquor gives the best results. The methods of producing level colors are: —

(1) Increasing the proportion of soap or boiled-off liquor.

(2) Diminishing the amount of sulphuric acid, or using a weaker acid.

(3) Regulating the temperature of the bath.

Alkali Colors. — With these dyes, the silk is dyed in a soap-bath, sometimes with the addition of soda or borax, and the color is afterward developed as in the case of wool.

CHAPTER XVIII

MORDANT DYESTUFFS

Mordant dyestuffs are acid bodies which are always fixed upon the fiber in the form of insoluble metallic salts. The most important and fastest natural dyes belong to this group, and also many of the most important artificial colors. The lakes in which the mordant dyes are fixed upon the fiber are often very complex in composition.

Mordant dyestuffs form insoluble calcium salts, so that, in many cases, hard water is injurious in dyeing with them.

Methods of Application. — The mordants used for these dyes consist of salts of iron, chromium, and aluminium. Three general methods of application are in use: —

(1) *Mordanting and dyeing*, used for cotton and wool. The goods are mordanted first, and then dyed. The mordant is fixed on cotton in various ways. Wool boiled in dilute solutions with metallic salts decomposes them, and when afterward brought in contact with the dyestuff, the metallic oxides held in the wool fiber combine with it to form colored lakes.

(2) *Single-bath method*, used for cotton and wool. The dyestuff and mordant are mixed in the same bath, and the color-lake is gradually formed, and absorbed by the fiber, in the manner of a direct dye.

(3) *Dyeing and mordanting*, used only on wool. The principle of this process is, that certain mordant dyes

possess such highly acid properties that they may be dyed upon wool in the same way as acid dyes, and the color-lake is afterward formed by application of the mordant in the same or a different bath. Dyes belonging to this group are called *acid-mordant colors.*

Natural Mordant Colors. — Most of the natural dyestuffs are members of this group. The more important are logwood, fustic, and cutch. They occur in commerce as the raw material, and as liquid or solid extracts.

Artificial Mordant Dyestuffs. — These dyes occur as: —

Powders, generally soluble in 20 to 50 times their weight of water. Some of the powders are compounds of insoluble mordant colors with sodium bisulphite, and must be dissolved in cold water, as hot water decomposes them.

Pastes, consisting of the dyestuffs in a finely divided form, mixed with water. They must not be allowed to dry up or freeze, as they thereby become less soluble. Vessels not perfectly closed may be covered with a damp cloth moistened with glycerol, to prevent evaporation. Pastes, damaged by drying or freezing, can be restored as follows: Dissolve in caustic soda, precipitate with a slight excess of sulphuric acid, wash the precipitated dye, and dilute with water.

Mordant Colors on Cotton. — The methods of applying mordant dyestuffs to cotton and wool are so entirely different that it is best to treat the two separately.

One of the mordant dyestuffs most important in cotton dyeing is alizarin.

Alizarin. — The use of madder root for dyeing has come up to us from the ancients. In 1826, madder was found to contain two coloring principles, alizarin and purpurin; in 1868, Graebe and Liebermann discovered their composition, and prepared both of them from anthracene, a hydrocarbon found in coal tar. Since then, artificial alizarin has driven madder root almost completely from commerce.

Alizarin, $C_{14}H_8O_4$, occurs as a reddish yellow powder, or as bright orange-red needles, or as a paste with water. It is almost insoluble in cold water, and very slightly soluble in hot water, but it dissolves readily in alcohol or ether and some other solvents. It dissolves in caustic soda, forming a sodium salt of a blue-violet color; also in ammonia (ammonium salt) with a purple color. Acids decompose these salts, and precipitate the alizarin. Like other dyes, it is reduced to colorless compounds by reducing agents.

Commercial alizarin is sold as a paste containing 20 per cent dry matter, representing nearly pure dyestuff, as a paste containing 40 per cent of dry matter, and as a powder containing 80 per cent or more of alizarin. Two essentially different shades of alizarin are distinguished, *alizarin V* (v = violet) or blue shade, and *alizarin G* (g = gelb = yellow) or yellow shade. Alizarin V is the purest commercial alizarin. Alizarin G is mainly a mixture of iso- and flavo-purpurin, containing some alizarin. It produces the most brilliant reds.

Alizarin forms a number of insoluble lakes with calcium, aluminium, etc.

Methods of Application. — Alizarin is applied to cotton by the following methods: —

(1) The Turkey-red processes, which yield exceedingly bright and fast reds. Oils and aluminium salts serve as mordants.

(2) Alizarin-red processes, in which the mordant is aluminium acetate.

(3) Chromium mordants, for claret-red and maroons.

(4) Iron mordants, for violets.

Turkey-red Processes. — Turkey-red is the brightest and fastest, and at the same time the most expensive, red which can be produced on cotton.

Like bleaching and other important processes, the methods for the production of Turkey-red vary in different mills, and according to the results desired.

Three processes for Turkey-red dyeing are in use. In all three, the material is treated with oil, which is fixed or made insoluble, and then caused to combine with the aluminium mordant, after which the dyeing follows. The difference lies in the use of different oils, and consequently different methods of fixing it.

The *emulsion* or old process uses rancid olive oil.

Steiner's process uses hot, clear olive oil.

The *new process* uses Turkey-red oil.

We will consider the last-named process only.

New Turkey-red Process. — The operations are as follows: —

(1) *Boiling Off.* — The yarn or cloth is boiled off with caustic soda.

(2) *Oil Preparing.* — The washed goods are hydro-extracted, but not dried, and are then worked in a bath

of 10 to 20 pounds neutralized Turkey-red oil (50 per cent) in 10 gal. water.

Turkey-red oil consists of a mixture of fatty acids and their sulphates prepared by treating castor oil with sulphuric acid, under suitable conditions, and partly neutralizing the product with soda or ammonia.

(3) *Stoving.* — The oiled goods are wrung evenly out and dried at a temperature of 40° to 60° C. The Turkey-red oil is decomposed, ammonium sulphate and fatty acids being produced, which latter are fixed on the fiber by chemical decomposition.

(4) *Aluming.* — The goods are worked 5 or 6 hours in a warm bath of aluminium acetate (red liquor), or of basic aluminium sulphate, wrung out, and dried. The basic aluminium sulphate is prepared by dissolving 4 parts alum in water, and adding to the cold solution 1 part crystallized sodium carbonate in solution. Aluminium compounds with the fatty acids are fixed on the fiber.

For the production of a bright and intense red, the second, third, and fourth processes are repeated.

(5) *Chalking.* — The material is worked in a bath of finely ground chalk, when the alumina is precipitated in a basic condition, *i.e.* "fixed." Phosphate of soda and ammonium carbonate are also used as fixing agents.

(6) *Dyeing.* — A bath is prepared with the desired quantity of dye (alizarin G), the goods entered at 25°, and turned 20 minutes; in half an hour the bath is heated to 60 or 70°, and maintained at this temperature for an hour. After dyeing, the goods are wrung out and dried, with or without washing.

It is essential that the dye-bath contain lime, though not too much. If the water used contains little or no lime, a suitable addition of ground and washed chalk may be made; a moderately hard water requires no addition. Very hard water, or water which contains iron, cannot be used in Turkey-red dyeing.

After dyeing, the goods possess a dull red color, which is transformed by the processes which follow into the brilliant Turkey-red shade.

(7) *Second Oil Preparing.* — The material is impregnated with a solution of neutralized Turkey-red oil, and dried. This is often omitted.

(8) *Steaming.* — To develop the color, the goods are steamed, with or without pressure.

(9) *Clearing.* — The goods are worked twice in a soap-bath, sometimes warm, sometimes boiling. This removes loosely fixed dye, and fixes the remainder more permanently.

Alizarin-red Processes. — The colors produced by these methods are cheaper, and inferior in brilliancy and in fastness to the Turkey-reds.

With Aluminium Acetate. — The processes follow: —

(1) Mordanting or padding with aluminium acetate.

(2) "Ageing" in a warm room, basic aluminium acetate being formed. If the temperature is too high, the decomposition goes too far, and the mordant is "burned."

(3) "Fixing" in a bath of phosphate, arsenate, or silicate of soda, which removes the remainder of the acetic acid. Wash.

(4) Dyeing in a bath containing Turkey-red oil, and sometimes some tannic acid as well as the dye. Wash and dry.

(5) Impregnation with Turkey-red oil, and drying.

(6) Steaming, soaping, and drying.

With Aluminate of Soda. — This process is usually applied to piece goods. The cotton is padded with aluminate of soda, dried, aged, and the aluminium fixed with ammonium chloride or silicate of soda, and then in a chalk-bath. It is then dyed, etc.

Aluminate of soda is prepared by dissolving aluminium hydroxide in caustic soda: —

$$Al(OH)_3 + 3\ NaOH = Al(ONa)_3 + 3\ H_2O.$$

Erban and Specht's Method. — (*a*) For dark shades. The material to be dyed is impregnated with a solution of the color in ammonia, and dried, whereby the volatile solvent escapes, and the coloring matter is deposited in an insoluble form upon the fiber. A second impregnation follows with aluminium-acetate, after which the material is steamed, which expels the acetic acid and fixes the color-lake upon the fiber.

(*b*) For light shades. The fiber is impregnated with a solution of aluminate of soda and the color in ammonia. The material is then steamed. If caustic soda is used, in any form, the steaming must be done with steam which is highly charged with acetic acid.

Alizarin on Chromium Mordants. — The shades produced are claret-red and maroon. Alizarin B or V may be used. The former gives more brilliant and bluer tints. The process of mordanting usually used is as follows: —

(1) Saturation once with a solution of neutralized Turkey-red oil, and drying.

(2) Impregnation with tannin.

(3) Mordanting with basic chromium chloride, chromium acetate, or chromium mordant GA I.

(4) Washing with weak lime-water.

(5) Dyeing. The goods are introduced in the cold dye-bath, which is heated gradually to boiling (in an hour), and boiled two hours. They are then well rinsed in water, and finally soaped at 60° or at the boil, washed and dried.

Methods rarely used are:—

Erban and Specht's Method.—A solution of chromium hydroxide in ammonia replaces sodium aluminate used in mordanting with aluminium.

Impregnation with Unstable Chromium Compounds.—In this case, the cotton is treated with a chromium compound which decomposes on the fiber, forming insoluble chromium hydroxide. The decomposition may take several hours. The cotton is then washed. The chromium compounds used are sodium chromite, chromium mordant GA I, and chromium bisulphite.

Sodium chromite is prepared by dissolving chromium hydroxide in caustic soda:—

$$Cr(OH)_3 + 3\,NaOH = Cr(ONa)_3 + 3\,H_2O.$$

Or by treating chrome alum or chromium acetate with a sufficient quantity of caustic soda solution to dissolve the precipitate first formed.

Double Decomposition of Chromium Salts with Soda.—The material is impregnated with a salt of chromium, preferably a basic salt, dried, and passed through a boiling solution of soda ash (sodium carbonate). Chromium hydroxide is precipitated:—

$$Cr_2(SO_4)_3 + 3\,Na_2CO_3 + 3\,H_2O = 2\,Cr(OH)_3 + 3\,Na_2SO_4 + 3\,CO_2.$$

The operations are repeated until sufficient chromium hydroxide has been deposited on the fiber. The chromium salts used are the sulphate, nitrate, chloride, acetate, or their basic salts, like $Cr_4(SO_4)_3(OH)_6$.

Alizarin on Iron Mordants. — Violet shades are produced by the use of iron mordants, alizarin V being used.

One method consists in oiling with Turkey-red oil, mordanting with pyrolignite of iron, fixing with a chalk-bath, and dyeing.

By a second method, the cotton is mordanted with tannin and iron, and fixed with a bath of cow-dung, or with arsenate, phosphate, or silicate of soda.

The dye-bath is made up with dyestuff and neutralized Turkey-red oil, the cotton introduced into the cold bath, and the temperature raised during 1½ hours to 75°. After dyeing, the cotton is washed, dried, steamed, and soaped.

Experiment 70. — Mordant a boiled-off skein of cotton yarn with 10 per cent alum and 2 per cent sodium carbonate in 200 cc. water, working 15 minutes. Squeeze, and work 10 minutes in 2 per cent chalk in 200 cc. water. Wash and dye as directed below.

Mordant a second skein by working 15 minutes in a solution of 25 per cent ferric sulphate in 200 cc. water. Squeeze, and pass through lime-water. Wash. Dye both skeins as follows: —

Prepare the bath with 20 per cent alizarin paste and 2 per cent chalk in 200 cc. water. Enter the cotton, work well, heat to boiling, and boil 30 minutes. Clear by boiling in a 1 per cent solution of soap.

Test fastness to washing. What class of colors is this dye in?

Logwood. — Logwood is a very important dye for the production of blacks on cotton. Its properties and chemistry have already been treated in Chapter V.

The methods for dyeing logwood on cotton are illustrated by Experiments 30 and 31 (mordanting and dyeing), and Experiment 33 (single-bath method). Variations of these methods are in use, one of which is as follows: —

The material is padded or steeped in an infusion on myrabolans (40 per cent), and squeezed; passed through weak lime-water, which forms calcium tannate; worked in "nitrate" of iron, or acetate of iron of 4° Tw.; passed through lime-water, which precipitates basic ferric tannate; washed thoroughly and dyed.

Logwood extract is usually employed in cotton dyeing. The cloth or yarn is dyed with 30 to 50 per cent logwood chips, or 5 to 8 pounds extract, usually with the addition of fustic (a yellow dye) to modify the shade, and also a little copper sulphate. The dyeing is commenced cold, and the temperature of the bath raised slowly to the boiling-point.

If the logwood black is to be very fast to washing, it is *saddened* after dyeing by passing through a hot, weak bath of potassium bichromate or nitrate of iron. In some cases the saddening is effected by adding ferrous sulphate to the dye-bath when the dyeing has been completed, and working about 20 minutes longer. The results are not as good as if a separate bath is used.

The single-bath method does not yield colors so fast to rubbing as the two-bath method.

Defects. — *Rubbing* is caused by too rapid fixation of the color, or by incomplete washing after mordanting. In the single-bath method, rubbing is due to superficial fixation of the color-lake.

Greening. — Logwood blacks sometimes become green after short usage; it is due to the use of too much bichromate of potash in the saddening bath.

Tendering is caused by the oxidation of the fiber by an excess of bichromate. *Rusty colors* are due to over-oxidation of the coloring matter.

Cutch. — Cutch, or catechu, is used for the production of browns on cotton. It is extracted from certain plants growing in India, and occurs as irregular lumps of a brown color.

Cutch contains a tannic acid known as catechu-tannic acid, which has a direct affinity for the cotton fiber. It is applied directly to the fiber, usually with the addition of a little copper sulphate. Potassium bichromate in a second bath produces the color-lake. For a full shade, the cotton is boiled with from 15 to 20 per cent cutch, and 1.5 to 2 per cent copper sulphate. After standing for some time, it is worked in a hot bath of 2 per cent bichromate of potash, washed, and dried.

Cutch is combined with logwood, fustic, and other mordant colors for compound shades; it can also be topped with basic colors, since it contains tannic acid.

Other Mordant Colors. — Other mordant colors are applied to cotton by the same methods as are used for alizarin, or logwood.

Bisulphate compounds of certain alizarin colors may be applied in the same bath with a chromium mordant; the material is dried, and then steamed, which decomposes the bisulphite compound, and the insoluble chromium lake is formed.

For example, cotton is evenly saturated with a solution of 10 lb. alizarin blue S in 8 gal. cold water, to which 1 gal. chromium acetate 32° Tw. is added. The cotton is dried, steamed, washed, soaped, and dried.

Alizarin indigo-blue S, alizarin green S, and cerulein S are applied in this way.

Mordant Dyestuffs on Linen. — Mordant colors are largely applied on linen. The methods are similar to those used for cotton.

Mordant Colors on Wool. — The mordant dyes are largely used on wool, the colors produced being very fast to air and light, dilute acids, alkalies, and to scouring.

A prime necessity in applying mordant colors to wool is the thorough purification of the fiber from fatty and greasy matter. Any of these form sticky soaps with the mordants, which attract dyestuff, and afterward rub off.

The mordant colors for wool are divided into two classes: ordinary mordant dyestuffs and acid mordant dyestuffs.

Ordinary Mordant Colors. — These are applied by mordanting and dyeing, and by the single-bath method. The mordants are salts of aluminium, chromium, and iron.

Mordanting with Aluminium. — Aluminium mordants are of limited application in wool dyeing, the only colors produced by its use being the alizarin reds and oranges, and alizarin maroon.

The bath is charged with alum and an assistant, whose function is to prevent the alum from decomposing too rapidly, so that good penetration and even mordanting will result. The assistants used are tartar (cream of tartar), oxalic acid, sulphuric acid, and lactic acid, tartar being preferred. The quantity of liquid in the bath should be between 30 and 50 times the weight of the wool. In too dilute solution, alum is decomposed too rapidly and fixed superficially, so that the colors are poor, and rub off. In too strong solution, the wool fixes too much acid along with the alumina, which hinders the lake formation during the subsequent dyeing process, so that the color produced is not very fast.

The goods are entered at a low temperature, the temperature raised gradually to the boil, and the bath boiled 1½ to 2 hours. The amount of alum and assistants to be used depends on the depth of color desired: 6 to 10 per cent of alum and 5 to 8 per cent of tartar. For an example, see Experiments 28 and 71.

For reds, neither the water nor the alum should contain even small quantities of iron, since it dulls the red. *Copper* should not come in contact with the bath for the same reason. The pipes for heating the bath may be of tin or tinned copper.

Mordanting with Chromium. — Chromium is largely applied for dyeing wool with mordant dyes. There are two methods of mordanting: —

(1) The wool is boiled with a solution of potassium bichromate and an assistant, which may be tartar, oxalic acid, lactic acid, or sulphuric acid. The function of the assistant is to liberate chromic acid, which is taken up by the fiber. Tartar, lactic acid, and oxalic acid reduce the greater portion of the chromic acid to chromium hydroxide, while, when sulphuric acid is used, only a small portion of the chromic acid is reduced by the wool itself. Wool, properly mordanted with potassium bichromate and tartar

or oxalic acid, is greenish in color, not yellow or brown. The different effect of the two assistants is shown clearly by Experiment 32.

(2) Chromium fluoride (2 to 4 per cent) is used with 1 to 2 per cent oxalic acid as an assistant. The chromium is fixed entirely in the form of chromium hydroxide.

After mordanting, the goods are often allowed to lie over night before washing, when the mordant "feeds," that is, is further decomposed and absorbed by the fiber. Piece goods and skeins should be washed after mordanting, and never allowed to hang on poles or rails over night, as the mordant will feed on excessively at the lower points, causing uneven colors. The goods mordanted by the first method should also be kept moist and protected from direct sunlight, since chromic acid would be reduced in the dried and exposed portions, thus strengthening the mordant and causing uneven colors.

Dyeing. — For *aluminium* mordants, the dye-bath should contain lime, preferably as calcium acetate, and an addition of tannic acid is said to improve the fastness of the colors. For a full shade, 7.5 per cent acetate of lime and 2 per cent tannic acid are used.

For *chromium* mordants, the dye-bath is made slightly acid with acetic acid before the color solution is added. The objects of the addition of acetic acid are as follows: —

(1) To correct the hardness of the water, and prevent the formation of insoluble calcium lakes.

(2) To neutralize alkali present in many dyestuffs.

(3) In slight excess, to facilitate the fixation of many dyestuffs.

The excess required is 2 per cent of the weight of wool over that required to neutralize the water and the alkali in the dye. Alizarin red, alizarin orange, alizarin brown, and gallein require a neutral bath, however, as the addition of acetic acid prevents the exhaustion of the bath.

In dyeing, the wool is worked for fifteen minutes without heating, and then the temperature is raised very slowly, so that the bath boils in about an hour. The boiling-point must not be reached before the bath is nearly decolorized. To develop the color, and fix it thoroughly, 1½ to 2 hours' boiling is required. If the boiling is not continued long enough, the color will rub.

EXPERIMENT 71. — *Chrome Mordant.* — Mordant a 5-gram wool skein by boiling half an hour in 3 per cent potassium bichromate and 2 per cent cream of tartar in 200 cc. water. What color is it? Dye in a bath of 10 per cent alizarin in 200 cc. water, boiling half an hour.

Mordant a skein as directed above and dye with 2 per cent anthracene acid brown N.

Mordant and dye with 2 per cent alizarin blue CS.

Test fastness to washing.

Alum Mordant. — Mordant a 5-gram skein of wool as follows: Boil half an hour with 6 per cent alum and 4 per cent sulphuric acid. Rinse, and dye with 10 per cent alizarin and ½ per cent chalk, boiling half an hour.

Test fastness to washing.

Saddening. — Full dark shades of certain colors, as alizarin brown, or alizarin red, may be saddened with ½ per cent bichromate of potash or 1 per cent copper sulphate, to make the colors faster to milling.

Level Dyeing. — Level dyeing is promoted: —

(1) *By regulating the Temperature.* — If the bath is heated up too rapidly, or the goods entered at too high

a temperature, the combination of dye and mordant takes place too rapidly, and uneven colors result.

(2) *Use of Alkalies.* — The alkalies form soluble salts with mordant colors, which are taken up very slowly by the mordanted wool; finally, by adding acetic acid, the bath is exhausted. For goods difficult to dye through, the following method is used: The dye-bath is charged with color and 2 to 3 per cent ammonia, the goods are then entered, the temperature raised to a boil, and acetic acid gradually added. In this manner, an equal penetration with the dyestuff is obtained and more level shades. Hard water should be purified for use in this process.

Defects in Dyeing. — Uneven dyeings may be due to uneven mordanting, caused by heating the mordant bath too rapidly, by the use of a too dilute mordant bath or too small a quantity of the assistant, or not working the goods sufficiently in the mordant bath. It may also be due to uneven dyeing. *Rubbing* may be due to the use of a too dilute mordanting solution, or not boiling long enough in the dye-bath.

Single-bath Method. — The results by this method are not as good as by the preceding method; there is also some precipitation of dyestuff in the form of insoluble lakes.

Alum Mordant. — For light shades of alizarin the bath is prepared with 3 per cent alum, 2 per cent oxalic acid, some calcium acetate, and the necessary amount of dyestuff. The wool is entered at a low temperature, and the temperature raised slowly. The oxalic acid holds the color-lake in solution until it can be absorbed by the wool.

Chromium Mordant. — A number of mordant colors which are not oxidized by chromic acid yield very good results by the single-bath method, using 3 per cent potassium bichromate and 2 per cent sulphuric acid for full shades.

Chromium fluoride is also used as a mordant.

Experiment 72. — Prepare a bath with 3 per cent alum, 2 per cent oxalic acid, $\frac{1}{2}$ per cent calcium acetate, and 10 per cent alizarin paste in 200 cc. water. Enter a 5-gram skein of woolen yarn, heat very slowly to boiling, and boil an hour. Test fastness to washing and rubbing.

Prepare a bath with 15 per cent alizarin and 3 per cent sodium bichromate, and dye as directed above. Test fastness to washing.

Mixing. — Ordinary mordant dyestuffs which require the same mordants, may be mixed and dyed in the same bath.

Logwood. — Logwood is an exceedingly important dye for wool dyeing, especially for the production of black. Examples of the methods of applying it are given in the experiments in Chapter V. For a high degree of fastness, the dyeing is saddened.

Acid-mordant Colors. — The acid-mordant colors are applied to wool in exactly the same way as the acid dyes, using the same precautions to obtain level dyeings. The bath is usually exhausted. The dyed wool is afterward treated with metallic salts, which develop the color by changing the dyestuffs into insoluble, dark-colored, and very fast compounds. In some cases the change is due to *oxidation* by bichromate of potash; in other cases a metallic salt or lake is formed. The mordanting operation may take place in the same bath as the dyeing, or in a separate bath.

Single-bath Method. — When the dye-bath is exhausted, it is allowed to cool to about 65°, the mordant is added, and the bath heated up again. The dyeings obtained by this process in the case of certain coloring matters are apt to rub and appear speckled, because that portion of the dye which was not taken up by the material is precipitated by the mordant as a lake, which is fixed superficially on the fiber.

Two-bath Method. — More time for entering and removing the goods is required, but the baths may be used continuously.

EXPERIMENT 73. — (*a*) Dye a 5-gram skein of wool with 3 per cent anthracene-acid yellow C and 5 per cent acetic acid in 200 cc. water, boiling half an hour. Rinse and mordant in a fresh bath with 1½ per cent potassium bichromate in 200 cc. water, boiling ½ hour.

(*b*) Dye with 2 per cent Cyprus green R, 5 per cent Glauber's salt, and 2 per cent acetic acid in 200 cc. water. Mordant with 1 per cent copper sulphate and 1 per cent acetic acid.

Test fastness to washing.

Mixing and Shading. — In mixing to produce compound shades, dyestuffs which require the same mordant must be used. For shading it is best to apply level-dyeing acid colors which are not affected by the mordant employed.

Mordant Colors on Silk. — The mordant colors are not applied extensively to silk, because they are more expensive to produce than other dyes, which, as a rule, are fast enough for all ordinary requirements. Silk has the power of decomposing mordants, and fixing the metal at the ordinary temperature.

Mordanting. — The silk is wetted out in the mordant solutions by continued handling, and then allowed to steep for several hours, or preferably over night. It is then wrung out, the mordant fixed if necessary, and finally it is washed thoroughly. The washing removes excess of acid, which tends to hinder the dyeing process, as well as any unfixed mordant which would cause the color to rub off. The mordant solutions may be freshened up and used continuously.

The mordants used are as follows: —

Aluminium Mordants. — (1) Basic aluminium sulphate is prepared by dissolving 10 oz. alum and 1 oz. soda crystals per gallon of water, and heating until the precipitate, which forms at first, has redissolved.

(2) Basic aluminium nitrate-acetate, or "nitrate mordant." The solution should be 10 to 15° Tw. The aluminium mordants are fixed by working, after mordanting, in a solution of silicate of soda of ½° Tw. for 15 minutes.

Chromium Mordants. — (1) Basic chromium chloride of 52° Tw. is used. Fix with silicate of soda.

(2) Chromium chromate. Chromium mordant GA III is diluted with four volumes water. Wash without fixing.

Iron Mordant. — Basic ferric sulphate ("nitrate of iron") is used. Wash without fixing.

Dyeing. — The dyeing is carried out in a bath containing ⅕ to ½ its volume of boiled-off liquor. For dark shades, the bath is made slightly acid with acetic acid; but since the addition of acetic acid accelerates the absorption of coloring matter enormously, acetic acid is not added for medium or pale shades, or irregular colors may be produced. The silk is entered cold, and worked cold half an hour, then the temperature is raised to near the boil in an hour. The dyeing is continued an hour longer; the silk is then washed, soaped, and brightened.

CHAPTER XIX

INSOLUBLE COLORS

THE insoluble colors constitute a group whose members have little in common. Some of them could be classed as mordant colors. They are all formed in an insoluble form on the fiber. This group falls naturally into three classes: —

(1) *Oxidation colors*, in which the dye is produced on the fiber by oxidation of soluble substances. Indigo, formed by the oxidation of indigo-white by the air, and aniline black, from aniline, are the members of this group.

(2) *Insoluble azo colors*, which are produced upon the fiber by the combination of a diazonium compound with other organic compounds. Paranitraniline red is the most important member of this class.

(3) *Mineral colors*, which are inorganic in nature, and are produced by chemical reaction directly upon the fiber. Examples: iron-buff, chrome-yellow.

Oxidation Colors. — Aniline black is produced on the fiber by the oxidation of aniline oil by oxidizing agents; indigo, by the oxidation of indigo-white by the air.

Aniline Black. — Aniline black is one of the most important black dyes. It became of commercial importance soon after 1860, when aniline could be purchased at a reasonable price. The composition of aniline black is not certainly known; it varies according to the method of dyeing. Three compounds have been separated from it:—

Emeraldine is the first product of oxidation. It is a green salt, the free base of which is blue.

Nigraniline is found by the oxidation of emeraldine. It is a violet-black base, the salts of which are green. Acids, especially sulphurous acid, turn it green.

Ungreenable black is formed by the oxidation of nigraniline under proper conditions. It is a black mass, and its color is not affected by acids or sulphurous acid. It combines with metallic oxides, such as chromic oxide.

Properties. — The chief constituents of aniline black are nigraniline and ungreenable black. If the former is present in any quantity, the black is changed to *green* by acids, especially sulphurous acid; and the same change takes place under use. To prevent "greening," all of the nigraniline must be oxidized to ungreenable black. The purer the aniline oil from which the aniline black is prepared, the more difficult it is to produce an ungreenable black. The less pure anilines do not, however, yield such a fine black as pure aniline.

Application. — Aniline black is extensively applied to cotton. Salts of chromic acid and chloric acid are used as oxidizing agents, there being also necessary, in the case of the latter, the presence of metallic salts, such as salts of iron, copper, and vanadium, to act as carriers of oxygen.

(*a*) *Single-bath Method.* — A mixture of aniline, acid, and chromates is prepared in such a manner that aniline black is slowly formed in solution, and the cotton gradually attracts the major portion of the color, for the most part mechanically.

(*b*) *Oxidation Black.* — In this case, the color is not developed in the bath. After the material has been impregnated with the solution of aniline and oxidizing agent, it is hung in a warm, moist room, where the oxidation takes place very slowly.

(*c*) *Steam Black.* — The color is developed very rapidly by a process of steaming.

There is considerable variation in the methods used for the production of an aniline black.

Production on Loose Cotton and Yarn. — Potassium or sodium bichromate is used as the oxidizing agent. Examples of the methods employed are as follows: —

(*a*) *Single-bath Method.* — For 100 lb. cotton use 10 lb. aniline oil, 15 lb. sodium bichromate, 40 lb. hydrochloric acid or 12 lb. sulphuric acid, and 160 gal. water. The dye-bath is filled with water, and the cold solution of aniline oil with a part of the hydrochloric acid is first added, then the bichromate dissolved in a small quantity of water, and lastly the acid. The cotton is introduced into the cold bath and turned continuously; when the color becomes distinct, the bath is slowly heated to 50 or 60° to develop the shade. The operation may last from 1 to 3 hours. If the heating has been too short, the black is liable to turn green under the influence of acids.

(*b*) *Steam Black.* — A steam black may be produced as follows: 6 lb. aniline, 9 lb. hydrochloric acid, and 12 lb. sulphuric acid are dissolved in 20 gal. water. Another solution of 12 lb. bichromate of soda and 20 gal. of water is prepared. After allowing to cool, 4 quarts at a time of each solution are poured into a small vessel, and the yarn is rapidly passed through the bath in lots of 2 lb., with fresh additions of the two solutions after each lot; within 1 or 2 minutes, the yarn becomes bronze-black. The material is then wrung out, and steamed 20 minutes at $3\frac{1}{2}$ lb. pressure, which process renders it jet-black and also ungreenable.

EXPERIMENT 74. — Dissolve 10 per cent aniline oil (which is dissolved in 12 per cent hydrochloric acid) in water, add 15 per cent sodium bichromate and 6 per cent sulphuric acid, and make the volume of the bath 200 cc. Enter the yarn, work well, heat slowly to boiling, and boil half an hour. The yarn is harsh to the touch. Soften by soaping it at the boil in a 1 per cent solution of soap.

Production on Cloth. — For cloth, the oxidizing agent usually used is sodium or potassium chlorate. Two processes are as follows: —

(1) Dissolve 10 lb. sodium chloride and 10 parts ammonium chloride in 8 gal. water. Dissolve 10 lb. copper sulphate in 7 gal. water. Dissolve 35 lb. aniline salt in as little hot water as possible, and neutralize the solution with a sufficient amount of aniline oil, testing the solution with litmus. When all the solutions are perfectly cool, add the solution of aniline salt to that of the sodium chloride and ammonium chloride, then add the copper sulphate solution, and dilute to 14° Tw. The cloth is then impregnated with the liquid, hydro-extracted, and aged or steamed. When the liquid becomes dark, it is replaced by fresh liquor; the old liquor is filtered, and used again for diluting fresh solutions.

After ageing, the goods are treated at 80° in a solution of 20 parts sodium bichromate, 5 parts soda, and 5 parts salt per 1000 parts water, washed, and steamed at 15 lb. pressure.

(2) Prepare concentrated solutions of 1¾ lb. aniline salt in 1 gal. water, and 1½ lb. ferrocyanide of potash in ¾ gal. water, and 1½ lb. potassium chlorate in 1½ gal. water. Work the cloth in a mixture of the solutions in a jigger; steam for two minutes; then work hot in a jigger in a solution of 1 lb. bichromate of soda in 50 gal. water, dry and finish.

Ageing Chamber. — Aniline black is usually aged in a special chamber (Fig. 20). The machine consists of a chamber provided with guide rollers for the cloth, and steam pipes for heating and for injecting steam. The cloth passes continuously through the apparatus.

Topping Aniline Black. — Aniline black is sometimes topped with a weak solution of methyl violet to render it ungreenable, the green and violet uniting to form blue. In order to avoid tendering, a black is often produced by dyeing a light aniline black and topping with other blacks.

Soaping. — Aniline black must be thoroughly soaped to soften the material. Soaping also neutralizes any traces of mineral acids which may not have been washed out.

Defects in Dyeing Aniline Black. — *Rubbing off* of the color is due to too rapid oxidation in the solution. *Greening* is due to imperfect oxidation of the aniline. *Tendering* is due to: (*a*) over-oxidation of the fiber by the oxidizing agents; (*b*) drying of the material during ageing or before the acid has been washed off; (*c*) imperfect final washing.

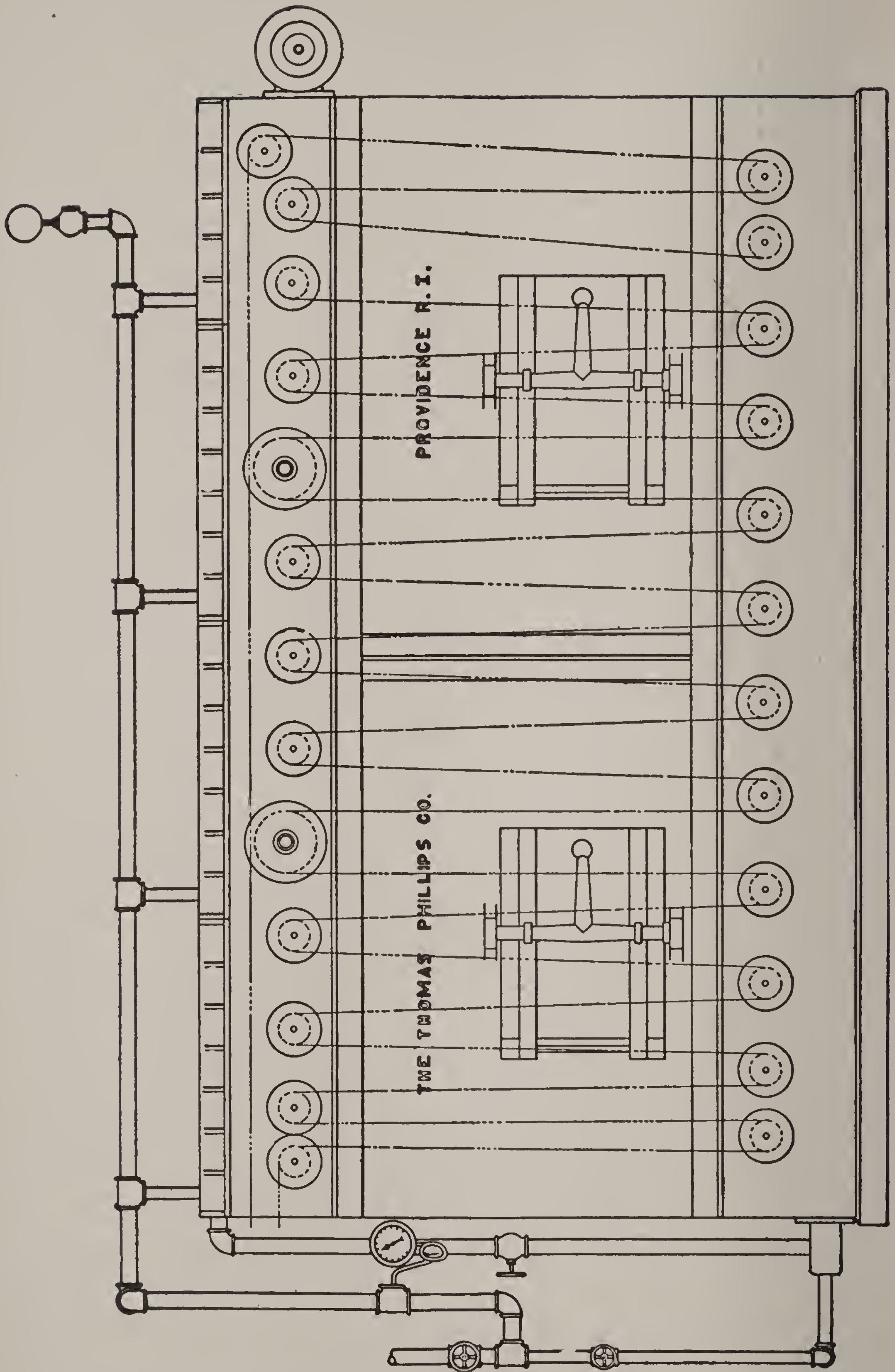

FIG. 20.—Aniline black ageing chamber.

Indigo. — Dyeing with indigo requires two operations: (1) preparing the indigo solution, or setting the vat, as it is called; (2) dyeing proper.

Application to Cotton. — Three methods for preparing an indigo vat for cotton are in use: namely, the lime-copperas vat, the zinc vat, and the bisulphite vat. In all cases, the indigo must first be ground to a fine paste with water. Artificial indigo is now put on the market in the paste form. The chemistry of these processes has been discussed in Chapter VI.

Copperas Vat. — As an example, the following is given: 4 lb. indigo are placed in 75 gal. water, 8 lb. copperas are then dissolved in it, and finally 10 lb. quicklime. The quantity of indigo varies from 2 to 7 lb. according to the shade to be produced, and the other ingredients are added in the same proportion. The vat is stirred well, and allowed to stand. In about 24 hours the vat should be in the proper condition for dyeing. If so, the liquor will be clear and of a brownish yellow color, and a bluish scum ("flurry") appears on its surface. If the liquid appears greenish, the indigo has not been completely reduced, and more lime and copperas should be added to the vat.

The copperas vat may be used about a month. If necessary, it may be strengthened by the addition of fresh quantities of indigo, lime, and copperas. When used up, the sediment is often dissolved in hydrochloric acid to recover the indigo which it usually contains.

Zinc Vat. — The zinc vat may be made up in the following proportions: Water, 1000 gal.; indigo, 30 lb.; zinc, 25 lb.; lime, 25 to 30 lb. The mixture is stirred well during a period of 18 hours, and then allowed to settle. Too much zinc keeps the vat muddy owing to the liberation of hydrogen. After a day's work its strength may be restored by the addition of fresh quantities of zinc, lime, and indigo.

Hyposulphite Vat. — In this case, the reducing agent is a hyposulphite, made by the action of zinc on sodium bisulphite. It is customary to prepare a strong solution of the reduced indigo, and add it to the bath as required.

Reduced Indigo. — Boil 20 lb. finely ground indigo with 20 gal. water, cool and add 25 lb. slaked lime in the form of a cream. Prepare a hyposulphite solution by mixing 80 lb. sodium bisulphite of 70° Tw. with 9 lb. zinc dust in a vessel kept cool by immersion in another vessel containing cold water. When the zinc has dissolved, the hyposulphite is run into the indigo and lime mixture. The whole is stirred well at intervals until the indigo has dissolved, made up to 50 gal., and kept in casks protected from the air. Reduced indigo is placed on the market by the manufacturers of synthetic indigo.

Preparing the Vat. — Water is run into the vat and heated to 50° or 60° C.; some hyposulphite solution, prepared as previously described, is added, and then slaked lime. Reduced indigo solution is added in proportion to the shade desired to dye, the mixture stirred well, and allowed to settle half an hour.

If the vat becomes oxidized, a little hyposulphite solution should be added until the yellow color of the solution is restored. The vat should be kept alkaline by the addition of a little lime from time to time. The vat is strengthened by the addition of reduced indigo when necessary. The solution of sodium hyposulphite does not keep.

The vat described above is the *lime-hyposulphite* vat. For the *soda-hyposulphite* vat, a solution of caustic soda is added to the hyposulphite solution, and caustic soda is used in place of lime in making up the vat.

Dyeing. — *Skeins* are usually dyed by hand. The indigo vat is made deep enough for all the sediment to sink below the reach of the skein. Any scum on the surface of the vat is raked to one side, the skein immersed and turned for a moment or two, wrung out, and hung up for the color to develop. The depth of shade produced depends on the strength of the vat and the time of immersion. A single dip suffices for light shades; for medium or dark shades, two or more dips are used, as a deep shade produced by a single dip rubs badly.

Warps are run through the vat on a frame similar to that used in warp-dyeing machines. Usually several indigo vats are used and the warp frame is arranged to travel on a rail, so that it may be moved from one vat to another as occasion requires.

Topping Indigo. — Indigo on cotton is sometimes topped with methyl violet or direct reds to get deeper as well as brighter and redder shades.

Application to Wool. — For indigo on wool, the hyposulphite vat and the fermentation vat are used.

In the latter, the reduction of indigo is effected by the fermentation of sugar from the starch of bran or flour, etc.

An example is as follows: —

For a vat of about 700 gal., 6 lb. madder, 6 lb. molasses, 15 lb. bran, 15 to 30 lb. soda, 10 to 15 lb. indigo (20 per cent), and 2 lb. slaked lime are added to the vat one by one; it is stirred well, and heated to 50° C. The vat is then covered up and allowed to rest a day; then again carefully stirred up, and again left to rest until the fermentation has reduced the indigo. This will be apparent by the change in color of the liquid from dull black to yellow. Lime is then added to check the fermentation, and the dyeing begins.

Insoluble Azo Colors. — The insoluble azo colors are dyes produced in an insoluble form directly upon the fiber, and are used almost exclusively for cotton. The difficulty in producing them is to obtain a color which will not rub. The most important of these colors is paranitraniline red.

Paranitraniline Red. — Paranitraniline red is produced by combining beta-naphthol on the fiber with the diazonium compound of paranitraniline hydrochloride in solution. The latter is prepared by treating paranitraniline hydrochloride with nitrous acid. There are two steps in the process: (1) impregnating and (2) developing.

Impregnating. — A solution of sodium beta-naphtholate is prepared by dissolving beta-naphthol in caustic soda. Turkey-red oil or castor-oil soap is usually added to the solution to make the color brighter. The cotton is evenly impregnated with the solution, wrung out, and dried in a special oven where there is no danger of contact with acid fumes, which would decompose the sodium beta-naphtholate and cause the dyeing to spot. After the material is dry, it should be developed as soon as possible, as sodium beta-naphtholate is oxidized by the air, with the production of brown substances, and consequent irregularity in the shade.

Yarn in skeins is impregnated in this solution in 2-pound lots at a time, as it is difficult to impregnate larger quantities evenly. A portion of the warm solution is placed in a wooden bowl, 2 lb. of yarn passed through, another portion of the solution added, and another lot of yarn passed through, until 100 lb. have been impregnated. The yarn is then passed through once more, wrung, wrapped in thin calico and hydro-extracted, and dried at 148° F. for $3\frac{1}{3}$ to 4 hours.

Warps and cloth require a special impregnating machine, somewhat similar to the padding machine.

Example. — *For 100 lb. yarn,* 2 lb. beta-naphthol are mixed with 0.7 lb. caustic soda and dissolved in 2 qt. boiling water; $5\frac{3}{4}$ lb. castor-oil soap are dissolved in 11 qt. boiling water; mix and dilute to 12 gal.

For cloth, $5\frac{1}{2}$ lb. beta-naphthol, 4 lb. caustic soda, and 22 lb. castor-oil soap are dissolved in 55 gal. water.

Developing. — The paranitraniline is dissolved in boiling distilled water with the addition of hydrochloric acid. Cold water is then added, which precipitates paranitraniline hydrochloride as a yellow paste. When the solution has thoroughly cooled, a solution of nitrite of soda is added. In about 10 minutes a clear solution of the diazonium compound results, which is kept as cool as possible. Just before the yarn or cloth is developed with this solution, the free hydrochloric acid (which prevents it from decomposing) is neutralized by the addition of a solution of sodium acetate.

Decomposition of the solution is indicated by the evolution of gas. If any free hydrochloric acid is present when the cloth is developed, the color will rub. The solution may be tested with paper colored with congo red; free hydrochloric acid turns it blue. An additional quantity of sodium acetate should be added in such a case.

The development takes place in the same way as the impregnation.

Example. — *For 100 lb. yarn*, dissolve 1⅞ lb. paranitraniline in 1½ gal. boiling water and 1¾ qt. hydrochloric acid of 32° Tw. Add 3¼ gal. cold water. When cold, add a solution of 1⅛ lb. sodium nitrite in 3 qt. water, with stirring. Dilute to 9½ gal. with cold water. In another vessel, 4 lb. sodium acetate are dissolved in 11 qt. water. For developing, 4 parts of the first solution and 1 part of the second are used.

For cloth the same proportions of materials are used.

EXPERIMENT 75. — Prepare a solution of 9 per cent beta-naphthol (which is dissolved in caustic soda) and 20 per cent sodium carbonate in 100 cc. water. Work in this a *boiled-off* skein of cotton for 5 minutes, remove, squeeze as evenly as possible, and dry.

After the yarn is dry, prepare a solution of 3 per cent paranitraniline hydrochloride and 2 per cent sodium nitrite, and add 10 per cent sodium acetate in a few moments.

Immediately enter the prepared yarn, remove, wash, and dry. Test fastness to washing. What is the color?

Soaping. — After dyeing, the goods are washed well in cold water, and soaped with 2 per cent soap, which removes the loosely adhering particles of color.

Defects. — Irregular or spotted dyeing may be caused by: (1) action of acid fumes upon the impregnated material;

(2) oxidation before developing, caused by slow drying or delay in developing; (3) uneven impregnation or uneven development. Unless properly applied, the color will rub.

Other Colors. — The other insoluble azo colors are produced in a similar way to paranitraniline red; but as they are rarely used in dyeing, they will not be mentioned further.

Mineral Colors. — Chrome-yellow, or lead chromate, has already been studied. Other mineral colors are manganese brown, iron-buff, and Prussian blue.

Manganese Brown. — Manganese brown is a hydrate of manganese peroxide, and is produced by precipitating manganese hydroxide on the fiber and oxidizing it: —

$$MnCl_2 + 2\ NaOH = Mn(OH)_2 + 2\ NaCl.$$

$$Mn(OH)_2 + O = MnO_3H_2.$$

The color is very fast to light and washing.

Production on Cotton. — The cotton is passed through a solution of manganous chloride which has been neutralized, if necessary, and then through a hot solution of caustic soda. It is then passed through a weak solution of chloride of lime or bichromate of potash to complete the oxidation.

Iron-buff and Nankin Yellow. — These are composed of hydrated ferric oxides. They are produced by precipitating a ferric salt on the fiber with an alkali or alkaline carbonate: —

$$Fe_2(SO_4)_3 + 6\ NaOH = 2\ Fe(OH)_3 + 3\ Na_2SO_4,$$

or by precipitating a ferrous salt in the same way, and oxidizing the ferrous hydroxide. The colors are fast to light and washing.

Production on Cotton. — The material is saturated with a solution of nitrate of iron (3° to 6° Tw.), and then passed through a weak solution of caustic soda, lime-water, or chalk. The two operations are repeated till a sufficient depth of color is produced.

Prussian Blue. — Prussian blue is ferric ferrocyanide. It is fairly fast to light and washing.

Production on Cotton. — The cotton is dyed iron-buff, and then passed through an acidified solution of potassium (or sodium) ferrocyanide (yellow prussiate of potash). The depth of color depends on the quantity of ferric oxide on the fiber.

Production on Wool. — The Prussian blue is formed by the decomposition of potassium ferrocyanide with acids. The wool is dyed in a bath of 10 per cent potassium ferrocyanide and 20 per cent sulphuric acid, boiling an hour. Prussian blue is formed, and absorbed by the wool.

CHAPTER XX

MERCERIZATION — ARTIFICIAL SILK

Mercerization (see Chapter VII) consists in the treatment of cotton with strong solutions of caustic soda followed by a thorough washing. Under ordinary conditions the cotton shrinks in length, but if the treatment and washing are conducted under tension, the cotton does not shrink, and receives an increased luster.

The applications of mercerization are as follows: —

(1) To produce embossed effects on cloth.
(2) To impart a luster to cotton (artificial silk).

Production of Embossed Effects. — Embossed or relief effects are produced upon cloth in two ways: —

(1) The design is woven with wool and cotton, and the cloth mercerized. The cotton contracts, causing the wool to stand out. The operation must be conducted at a low temperature to avoid injuring the wool.

(2) The caustic soda is printed upon the cloth in stripes or other designs. The printed parts contract, causing the other parts to appear in relief. If afterward dyed, the mercerized fibers take up more of the dye than the other portions, producing a colored design. A variation is to print the cloth with something which will protect it from the action of caustic soda, such as wax or oil, and then mercerize the cloth.

Production of Lustered Cotton. — The most important application is to impart a luster to cotton. The yarn is mercerized under tension. The conditions which influence the production of the luster are as follows: —

(1) *Quality of the Cotton.* — The higher the quality of the cotton the better the luster. While all cotton increases in luster, the most silky appearance is imparted to high grades, as Sea Island and Egyptian.

(2) *Twist of the Cotton.* — A soft twist is more favorable than a hard twist.

(3) *The greater the tendency to contract, and the more effectually contraction is prevented, the better the luster.* — More tension than is required to prevent contraction is not necessary, and may result in rupture of yarn or cloth. The factors which influence the contraction are as follows: —

(*a*) The degree of contraction depends upon the strength of the mercerizing liquid: —

Specific gravity . . .	1.07	1.11	1.19	1.25
Contraction, per cent .	1	16	22	23

(*b*) The contraction decreases as the temperature rises: —

Temperature . . .	18° C.	30° C.	80° C.
Contraction, per cent	22	22	15

(*c*) The time of contact has little effect.

(4) *Mechanical manipulation*, such as beating, pressing, etc., are of no value.

(5) *Uneven mercerization* will take place if the material is not completely saturated with the caustic soda; if such goods are dyed, it is almost impossible to get a uniform color.

Process of Mercerization. — The cotton is first thoroughly wetted out, and then brought in contact with caustic soda of from 1.11 to 1.20 sp. gr., in appropriate apparatus for a few minutes, removed, and washed carefully. In most cases, the last traces of alkali are neutralized with a little acid. The first wash waters should be saved and used in preparing fresh solutions of caustic soda.

Machinery for Mercerizing. — Machines for mercerizing should impregnate the material as evenly as possible with the mercerizing liquid, and prevent contraction as far as possible; a large number of machines have been patented. For even mercerization, it is essential that the material should be carefully wetted out.

Skeins. — Machines for mercerizing skeins are of two types: —

(*a*) The first type consists essentially of pairs of iron rods on which the skeins are placed, and which are then moved apart until the desired tension is obtained. The skeins are then immersed in the mercerizing liquid. The rods are made to revolve in the caustic soda, so that all portions of the yarn will come in contact with the mercerizing liquid. After mercerizing and washing, the yarn is removed.

(*b*) The skeins are placed over a circular, perforated drum, which can revolve at a high rate of speed, and is surrounded by a mantle. The drum is revolved, and caustic soda solution introduced; the centrifugal force causes it to penetrate all parts of the yarn. The yarn is then washed with water and removed. This machine allows some contraction to take place.

Warps. — The machine resembles a warp-dyeing machine with two compartments, but is provided with a pair of heavy rollers where the warp enters, whose pressure may be regulated by a lever and weights to produce the desired tension. Each compartment is provided with a pair of squeezing rollers. The warps are pulled between the tension rollers by the squeezing rollers, through the solution of caustic soda, between the squeeze rollers and through the second compartment, which contains rinsing water, and between the final squeezing rollers. A jet of water just before the last pair of rollers aids in complete washing.

Cloth Mercerizing. — The cloth is wound on a roller, and passes through one pair of rollers into the caustic soda, through a second pair of squeeze rollers into water, through a third pair, then is wound on another roller. The tension of the rollers is adjusted so that the material cannot contract.

Properties of Lustered Cotton. — Cotton mercerized under tension (lustered) and without tension is the same chemically and, with a few differences, physically.

Lustered cotton is stronger than ordinary cotton, but weaker than cotton mercerized without tension. The effect of the tension is shown in the microscopic appearance of the fiber. Lustered cotton appears as a straight, translucent tube, with a small, round central opening. The luster is probably due to the fact that the surface of the cotton becomes smooth, thereby reflecting light in one direction instead of scattering it.

Mercerized cotton has a much greater affinity for dyes and mordants than ordinary cotton.

Dyeing Mercerized Cotton. — Mercerized cotton has a much greater affinity for dyestuffs, and absorbs them more rapidly and more completely from solution, than ordinary cotton. It also requires a smaller quantity of dye, from 30 to 40 per cent less with dark shades (see Exps. 46, 47, 48). Mercerized cotton is usually dyed with direct cotton colors, since these affect its luster least.

On account of its affinity for dyes, precaution must be taken that the color is not absorbed too rapidly, producing uneven shades.

Direct Cotton Colors. — The bath is made up with the dye and a portion of the salts required; the material is entered into the lukewarm bath, worked for about 20 minutes, then the remainder of the salts are added, and the dyeing finished in a bath heated from 40° C. to boiling, according to the depth of color. Turkey-red oil added to the bath assists in producing level colors.

Basic Colors. — These produce more brilliant colors than the direct cotton colors. The mordanting takes place as usual, excepting that from one-quarter to one-third less tannic acid or antimony salt than for ordinary cotton must be used, owing to the greater affinity of the mercerized cotton for tannic acid. The yarn should be washed well before dyeing.

To produce level colors, the dyeing must be conducted in a cold bath, acidified with acetic acid; it is also well to add the dyestuffs in two or three portions.

In dark shades, the exhaustion of the dye-bath may be completed by heating it to 50° or 60° C. toward the end of the operation.

Scroop Feel. — It is sometimes desirable to impart to mercerized goods the "scroop" feel of silk. Bleached yarn receives this property more easily than unbleached.

(1) *Bleached Yarn.* — The yarn is worked in a cold soap-bath, passed through water, worked several times in water strongly acidified with acetic or tartaric acid, and dried without washing.

(2) *Unbleached yarn* is treated with pure calcium acetate, then worked in a soap-bath, and finally in a bath containing acetic acid.

Level Dyeing. — The following circumstances aid in level dyeing: —

(1) *Even Mercerization.* — It is impossible to dye evenly material which has been mercerized unevenly.

(2) *Raising the Temperature of the Bath slowly.* — The rate of absorption of the dyestuff increases with the temperature.

Artificial Silk. — Two varieties of artificial silk are assuming commercial importance: namely, *cellulose* silk prepared from cellulose, and *gelatin* silk, from gelatine.

In spinning the fiber, the solution of the material is forced through very fine tubes; it is caught on an endless belt, and solidifies. The fineness of the tubes and the rate of motion of the belt regulate the size of the fiber.

Cellulose Silk. — The most important process for the manufacturing of artificial silk, and the one which has found the widest practical application, is the Lehner or Chardonnet process.

Cotton is first converted into nitro-cellulose (Chapter VII) by treatment with a mixture of sulphuric and nitric acids, and dissolved in a mixture of alcohol and ether. The solution is forced through fine glass tubes, when the solvent evaporates, leaving a fine thread of nitro-cellulose. It is dried in a warm room, and, since nitro-cellulose is very inflammable (guncotton), it is denitrated or converted into cellulose by treatment with ammonium sulphide.

Properties. — Collodion silk, as it is sometimes called, is a silk-like substance with a high luster and soft feel. It contains very little nitrogen. When wetted, it swells up and becomes very soft and weak, and it must be handled with caution in dyeing.

Dyeing. — Cellulose silk has a great affinity for direct colors and basic colors, and precautions are necessary for obtaining level colors. Direct cotton colors are applied with the addition of soap and soda, or Turkey-red oil.

Basic colors do not require a mordant. They are applied in a cold or warm bath (60° C.). To produce level dyeings, the solution of the dye should be added in several portions, and the absorption retarded by the addition of 1 to 3 per cent acetic acid.

Detection. — Cellulose silk may readily be detected in silk or wool by boiling the material with a solution of caustic potash. Silk or wool dissolves, but cellulose silk does not dissolve, even after prolonged boiling.

Gelatin Silk. — This is spun from a solution of gelatine in hot water. When the threads are dry, they are exposed to vapors of formaldehyde, which combines with the gelatine and renders it insoluble in water.

The fiber has a high luster. Like cellulose silk, it tears with the greatest readiness when wet.

CHAPTER XXI

DYEING OF UNION GOODS

The methods of dyeing goods composed of two or more kinds of fibers vary according to the effect desired and according to the character of the goods. It may be desired (1) to produce a uniform color, or (2) to produce different colors on the two fibers (two-colored effects or changeants). The three classes of material to be dyed are cotton and wool, cotton and silk, and wool and silk. The dyeing may take place in a single bath, or by means of two baths, one of which dyes one fiber more or less completely, and the other completes the dyeing.

The *direct colors for each class* may be divided into groups according to their behavior to both fibers in the same bath; the members of the group depend upon the class of material to be dyed, and to some extent upon the conditions of application.

As an example of the classification, the grouping of the colors for dyeing cotton-wool goods is given: —

Group I. Colors which dye both cotton and wool the same shade.

Group II. Colors which dye cotton a deeper shade than wool.

Group III. Colors which dye wool deeper than cotton.

Group IV. Colors which dye cotton and wool different *hues*.

Group V. Acid colors which dye wool in a neutral bath without dyeing cotton.

The affinity of the dye for one or the other fiber may be controlled to a great extent by varying the temperature of the dye-bath, etc.

Experiment 76. — Group I. Make up a bath of 2 per cent Chicago blue 6 B and 10 per cent Glauber's salt in 400 cc. water. Dye a 10-gram skein of cotton and a 5-gram skein of wool in the same bath. Dye half an hour at a temperature near the boil.

The cotton and wool are dyed nearly alike. By regulating the temperature, both fibers may be caused to assume the same shade.

Group II. Dye with 2 per cent curcumine S and 10 per cent Glauber's salt in a boiling bath. Dye as directed above. The cotton is dyed darker than the wool.

Group III. Dye with 2 per cent congo orange R and 10 per cent Glauber's salt in a boiling bath. The wool is dyed darker than the cotton. By dyeing at a lower temperature, equal colors may be produced on the two fibers.

Group IV. Dye with 2 per cent zambesi black F and 10 per cent Glauber's salt. The wool and cotton are dyed different shades.

These dyes are all direct cotton colors.

Cotton-wool Goods. — The following methods are available: —

(1) Dye the cotton and wool in the same bath with direct colors (direct cotton colors, alone or mixed with acid colors which dye wool in a neutral bath).

(2) Dye the wool with acid colors, then the cotton with direct cotton colors. The cotton can be topped with basic colors in the same or a different bath.

(3) Dye the cotton, then dye the wool with acid colors. This method is called *cross-dyeing* in an acid bath, and the

colors on the cotton must have great fastness to boiling water and acids.

(4) Dye the wool with acid colors, mordant the cotton, and dye with basic colors.

(5) Mordant the cotton, and dye cotton and wool with basic colors.

Dyeing with Direct Colors. — The rapidity with which the direct colors go on the fibers varies with the conditions, as follows: —

(1) The higher the temperature of the dye-bath, and the stronger the boiling, the deeper will the wool be dyed.

(2) The lower the temperature of the bath, the stronger will the cotton be dyed.

(3) The affinity of the direct cotton colors to wool can be diminished by an addition of soda or borax to the bath.

The baths do not exhaust, and should be kept as concentrated as possible.

Application. (1) *Dyeing the Cotton and Wool the Same Color.* — Dyes are used which dye the cotton and wool the same shade (Group I), or a combination of dyes which dye cotton deeper than wool (Group II), and those dyeing wool deeper than cotton (Group III). The bath is prepared with 3 oz. calcined Glauber's salt per gallon water. The dye-bath is boiled, steam is shut off, the material entered, and run one-half to three-quarters of an hour without steam. A sample is then examined. If the shades of the cotton and wool are both too light, another addition of the dyestuffs used for each fiber is made. The bath is then boiled up again, and the material worked another quarter to one-half an hour; a second sample is then taken. Should the wool appear too light, or of a different hue from the cotton, add some of the dyestuffs used for shading the wool (Group V), and boil up again. If the cotton is too light, or off color, the dyestuffs necessary for the cotton (Group II) are added, without raising the temperature. In dyeing deep shades, it is better to add one-fourth the dyestuffs at a time, as the wool may take them up too rapidly otherwise.

(2) *Dyeing the Cotton and Wool Different Colors.* — The wool is first dyed in boiling solution with acid dyes which dye in a neutral bath (Group V), then steam is shut off, and the cotton dyed with dyestuffs of Group II. Or dye directly with a mixture of colors of Groups II and V at 80° to 90°.

Acid Dyes. — Acid dyes which dye wool only are used in union dyeing. The cotton is dyed by means of other colors. The methods are used mostly for two-color effects.

Method 1. — The wool is dyed in a boiling bath (acid) with acid dyes which do not dye cotton, rinsed in a bath containing a little ammonia, and the cotton dyed with direct cotton colors which do not dye wool (Group II). The colors may be topped with basic dyes.

Method 2. — The cotton is dyed with direct cotton colors, diazotized, and developed, and soaped. The wool is then dyed with acid dyes in an acid bath. Other dyes sufficiently fast may be used for the cotton, such as Turkey-red.

Basic Colors. — The methods are: (1) The cotton is mordanted, and both wool and cotton dyed with basic dyes in a warm bath. Janus colors may be used to dye both wool and cotton in a neutral bath; the basic color is then fixed on the cotton in a bath of sulphuric acid, tannic acid, and tartar emetic.

(2) The wool is dyed with acid dyes, washed, and the cotton mordanted, and then dyed in a cold bath. The full depth of color must not be given the wool by the acid dyes, as it has a slight affinity for the basic colors in cold solutions, and its color is somewhat deepened in the second bath.

The cotton is mordanted in the usual way when it is to be dyed with basic colors, excepting that the temperature of the tannin bath should not exceed 45°; if it does, the wool fiber takes up some tannic acid, and the cotton comes out too light a color. The dyeing is effected in a neutral or slightly acid bath; the goods are entered at about 40°, and the temperature gradually raised to the boil.

With the Janus colors, the bath is prepared with 5 per cent zinc sulphate; after working the goods at the boil for five minutes, the solution of the dyes is added; in about 20 minutes, 20 per cent Glauber's salt is added, and the working continued an hour, or until the bath is nearly exhausted. The goods are then entered in a bath of sumac or tannin; after about 15 minutes, tartar emetic and sulphuric acid are added, and the bath warmed to 70°.

Shoddy Dyeing. — Cotton-wool goods may be prepared from fresh stock, or from shoddy, in whole or in part. When soft woolen rags are shredded for the purpose of remanufacture, the product is *shoddy;* it is always colored, and contains cotton thread. The cotton which has been twisted into knots, which happens often, is called *burls*.

In order to produce light shades upon dark shoddy, the material can be stripped in several ways: by boiling with 3 to 6 per cent sulphuric acid; by boiling with 6 to 12 per cent sulphuric acid and 3 to 6 per cent potassium bichromate, which oxidizes the color; or by reducing the color with hyposulphite of soda. In the latter case, two to three gallons hyposulphite solution (page 228) and one-half gallon acetic acid are mixed with a hundred gallons water. Which of these methods is to be preferred in any particular case depends upon the nature of the dye.

The following are the principal classes of shoddy cloths met with on the market: —

(1) Pure cotton warp with more or less dark shoddy weft. In dyeing these, it is chiefly a question of dyeing the cotton so as to make it invisible.

(2) More or less shoddy under-weft with pure woolen face, or with union face. In dyeing these, it is a question of covering the cotton burls, which mostly appear on the back, so that they will appear as little as possible. It is sometimes very difficult to dye the burls properly, and it has then been found advisable to pick them out with burling irons. In black dyeing, logwood on tannic acid and iron covers the burls very successfully.

Methods of shoddy dyeing are otherwise the same as for other union goods.

Cotton and Silk. — The dyes for cotton and silk are divided into four groups, Group V being eliminated. The direct colors are, as a rule, dyed in a soap-bath with the addition of phosphate of soda, Glauber's salt, or common salt, and a little soda. The addition of Glauber's salt causes the dye to go on the fiber more rapidly, and facilitates exhaustion of the bath; for pale shades, it is omitted. The addition of soap diminishes the rapidity of absorption of the dyestuff, and a large quantity of soap tends to leave the silk much lighter than the cotton. To obtain level dyeings with pale shades, the temperature of the bath must be raised very gradually. After dyeing, the silk is *brightened* with acetic acid.

The desired shade is seldom obtained without topping with acid or basic colors. Basic colors dye both cotton and silk; acid colors dye the silk only. The topping is conducted in a bath slightly acidified with acetic acid, which should be cold or slightly warm for basic colors, and about 45° C. for acid colors.

Two-colored effects are produced (1) by dyeing with direct cotton colors, which dye cotton and silk different colors, and (2) by dyeing the cotton, diazotizing and developing, and dyeing the silk with acid dyes.

Wool and Silk. — For this class of dyeing, colors are divided into the following groups: —

Group I. Colors which dye wool and silk the same shade.

Group II. Colors which, in a boiling bath, dye wool deeper than silk.

Group III. Colors which dye the silk in a cold bath without dyeing the wool perceptibly.

Group IV. Colors which dye the wool and silk the same shade in a cold or slightly warm bath.

Methods of Dyeing. — The acid dyes of Group I dye wool more rapidly at a boiling temperature, silk better at about 60° C.

The following methods are based on this circumstance:—

(1) Make up the bath with one-half of the dye, enter the goods at 60° C., bring to a boil, and boil about 15 minutes. The dye goes mostly on the wool. Shut off steam, and add the remainder of the dye when the temperature reaches 60° C., and work a half hour, when the silk will be covered.

(2) Add all the dyestuffs to the bath, and dye the wool as directed above. Then top the silk with basic dyes at 60° C.

(3) Dye as directed above, and dye the silk in a cold acid bath with colors of Group III.

A few colors are dyed in a bath made alkaline with sodium phosphate, and containing soap. Alkali blue must be developed after dyeing.

Direct cotton colors are dyed at the boil in a neutral bath with the addition of Glauber's salt. Should the silk remain too light, the goods are allowed to cool in the bath, or are topped in a fresh bath with colors of Group III.

For changeants, the wool is dyed first in a boiling bath with colors of Group II, and the silk dyed in a cold bath with colors of Group III.

CHAPTER XXII

DYE MIXING — DYE TESTING

The Solar Spectrum. — White light, when passed through a prism, is decomposed into a band of many different colored rays, called a spectrum. A *spectroscope* is an instrument for decomposing light into its components, and consists of three parts: a tube provided with a narrow slit through which the light enters, and containing lenses for making the rays parallel, a prism for decomposing the light, and a telescope for magnifying the spectrum. In the direct-vision spectroscope, all these parts are inclosed in a straight tube.

If sunlight is examined through a spectroscope, a number of dark lines are seen to cross the spectrum, which never vary in position, and serve to mark the position of colors. The colors in the spectrum, in the order in which they come, are as follows: —

Red, orange-red, orange, orange-yellow, yellow, greenish yellow, yellow green, green, and blue green, cyan blue, blue, blue violet, and violet. None of these rays of light can be further decomposed. Figure 21 represents the solar spectrum, showing the relative position of the fixed lines.

Absorption-spectrum. — If a solution of a colored body is placed before the slit of a spectroscope, some of the rays of light are absorbed, or quenched, and the result is the absorption spectrum of that solution. An absorption-spectrum may be represented by shading the portion of the spectrum which is absent. Figure 22 represents the absorption-spectrum of picric acid, a yellow dye. The solution of picric acid is yellow, not because it transmits yellow light only but for the reason that all the light which passes through the solution combines in the eye to produce the sensation of yellow. The same is true of other colored bodies. Two solutions may appear the same color, but have different absorption-spectra. They may transmit different rays of light which combine to produce the same color.

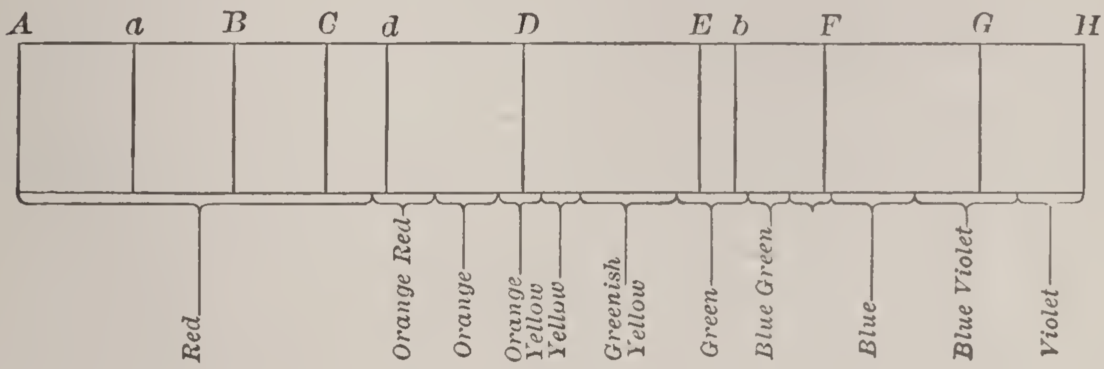

FIG. 21.—Solar spectrum.

A colored fabric behaves toward light exactly as if it were a colored solution. That is, a dye on a cloth has nearly the same absorption-spectrum as a solution of the dye of corresponding strength.

Dichroism. — The absorption-spectrum of a colored solution depends upon the strength of the solution used, or the thickness of the layer through which the light passes. A dilute solution usually allows more rays of light to pass through than a strong one; consequently the color of a solution may change according to its dilution. Chromic chloride is green in dilute solutions or thin layers, a claret-red in strong solutions or deep layers. Many dyes behave in a similar way. Methyl violet is bluish violet in dilute solution, claret in deep solution. Magenta is bluish pink in dilute solutions, red in strong solutions. Malachite green is blue green in dilute solution, reddish purple in very strong solution. This phenomenon is called *dichroism*.

The same effects of selective absorption are observed when colors are dyed upon fabrics. Thus, it will be often found that reds, when diluted to make tints, assume an orange cast, and blues become greenish blues or reddish blues.

Primary, Secondary, and Complementary Colors. — The human eye can distinguish but three simple or primary color-sensations: namely, red, blue, and green. All other colors can be considered as produced by admixture of these, and are called *secondary* colors. A mixture of red light and blue light produces violet light; blue lights and green lights produce blue green; and red light and green light produces yellow. All three combine to make white.

Complementary colors are two colors which when combined produce white. Every color which exists has its complementary color. The following pairs of colors are examples of complementaries: —

Red and green blue,
Orange and deep blue,
Yellow and ultramarine blue,
Green and red violet or purple.

Hue, Tint, Shade, Purity. — The meanings of these terms, as used in exact color nomenclature, are as follows: —

Hue is that which is generally understood by the term *color*, as red, yellow, blue, etc.

Purity. — By the purity of a color is meant its freedom from white, or any other color, as a pure yellow, a pure blue.

Tint. — The addition of successive quantities of white to a color produces a series of tints; there should be no variation in the hue of the color. Pink is a tint of red; cream, a tint of orange-yellow.

Shade. — The addition of black to a color produces a shade. Maroon is a shade of red; olive, a shade of yellow green. Shades may be reduced by that addition of white, with the production of corresponding tints, as tints of maroon, brown, etc.

Absorption-spectrum of Mixtures. — When two colored solutions are mixed together, the resulting color is that which is transmitted by both colors in common. Thus, when yellow and blue dyes are mixed, green is produced, because green is the only color transmitted by each, all the others being more or less absorbed or quenched. This is illustrated by Figure 22, showing the absorption-spectrum of a blue dye (indigo extract), and a yellow dye (picric acid), and the green produced by their mixture. The yellow dye transmits not only yellow but also red, orange, and green rays of light; the blue transmits blue and varying proportions of green, violet, and a little red light. Green is the only color common to both of them, and therefore freely transmitted.

The color which will be produced by the mixture of two dyes depends, therefore, upon their absorption spectrum, and is due to the combination of the rays of light which both dyes transmit. The color of the dye, while a guide, is no certain index to its absorption-spectrum, since two yellows, for example, may appear exactly alike, and yet absorb different rays of light. Mixed with the same blue, they will necessarily produce a different green. General principles, based on the color of the dye, may be laid down as an aid in their mixing, but there are only two ways to ascertain the exact color which will be produced: an examination of the absorption-spectrum of the dyes, or experimental dye-trials with the mixture.

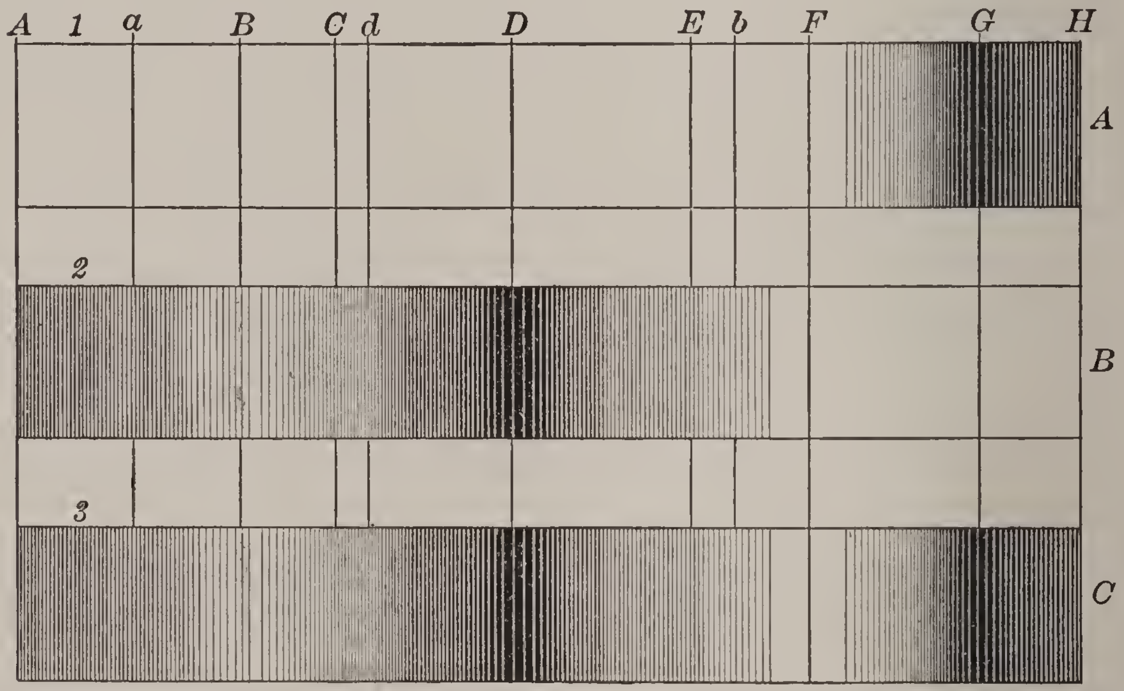

FIG. 22.—Absorption spectrum of a yellow dye (*A*), a blue dye (*B*), and their mixture (*C*).

Primary and Secondary Mixing-colors. — Experiments with dyes and pigments, which are explained by a study of their absorption-spectra, show that the following colors are produced by mixtures: —

Red + yellow produces orange.
Yellow + blue produces green.
Blue + red produces violet.

By varying the proportions of the red, yellow, or blue, innumerable gradations of hue can be obtained; thus, in the case of green, a series can be made ranging from yellow green on one hand to a green yellow on the other: —

3 Yellow + blue = green yellow.
2 Yellow + blue = yellow green.
Yellow + blue = green.
Yellow + 2 blue = blue green.
Yellow + 3 blue = green blue.

Similar variations may be made with the other colors.

Red, yellow, and blue are the *primary mixing-colors*, while red, green, and blue are the primary colors. The difference is due to the fact that in one case we deal with the colors produced by the mixture of colored lights, and in the other case with the light transmitted by colored solutions. Red, yellow, and blue dyes mixed produce a black; red, green, and blue lights combine to form a white light.

Mixing of Dyes. — The following considerations are only aids in color mixing. Spectroscopic examination or dyeing tests are necessary, as it is well known that two blues apparently similar may give with a yellow two greens of a very different cast.

Green. — The most brilliant greens are produced by the use of a greenish blue with a greenish yellow. A reddish blue or yellow of an orange cast gives dulled greens, — citrine, etc.

Orange is best produced by combining a yellowish red (scarlet) with a yellow without a green cast. The purest oranges are not made by mixture.

Violet. — Red of a bluish cast and blue of a reddish cast produce the best violet. Any yellow present dulls the color. The purest tones are obtained without mixture.

Shades. — By mixing the three primary mixing-colors, shades of the different hues are obtained, the colors depending upon which primaries predominate. In mixing colors to produce shades, it is better to employ dull, sad colors than clear and decided primary colors, as the slightest excess of any one of the latter causes a great alteration in the mixed shade. Shades compounded of dull hues are more easily matched and kept on the proper standard. It is also desirable to use as few color constituents as possible to produce the desired result, as a variety of coloring matters produces complexity when the shade requires to be matched or altered to a desired standard. More than three or four colors is not necessary to produce any shade that may be wanted.

The following are the principal shades produced by mixing colors with black: —

Maroon from red; russet from orange; brown from orange-yellow; olive from yellowish green; sage from green; slate from blue; lavender from violet; plum from purple.

As examples of color mixing to produce shades, the following are given: —

Red dyes mixed, in varying quantity, with black or green yield shades of red, ranging from claret through maroon to red black.

Plum, brown, and olive are obtained by mixing orange, red, and green in various proportions.

Olive is obtained by combining yellow, green, and orange.

Tints. — Tints are produced by lowering the percentage of dyestuffs used. In making a series of tints, it will often be found that the *hue* changes, which must be corrected.

Experiment 77. — (*a*) Dye cotton yarn with 1 per cent diamine red B, 1 per cent chrysamin G, and 3 per cent diamine blue 3 B with 20 per cent salt in 200 cc. water. Boil half an hour. Explain result.

(*b*) Dye with 1 per cent chrysophenin G, 1 per cent diamine blue 3 B, and 20 per cent salt.

(*c*) Dye with 1 per cent chrysophenin G, 1 per cent Chicago blue 4 R, and 20 per cent salt.

(*d*) Dye with 1 per cent congo orange R, 1 per cent Chicago blue 4 R, and 20 per cent salt.

(*e*) Dye with 1 per cent diamine red, 1 per cent chrysophenin G, and 15 per cent salt.

(*f*) Dye with 1 per cent diamine red, 1 per cent diamine blue 3 B, and 15 per cent salt.

(*g*) Dye with 1 per cent catechu brown, ½ per cent diamine blue 3 B, and 15 per cent salt.

Test fastness to washing of all the dyeings, and explain results. All the dyes named above are direct cotton colors.

Effect of Light on Colors. — Colored bodies reflect only the light which they receive; if the color of the light varies, their color will vary. If a series of the most beautiful colors is viewed by a pure yellow light, — such as may be obtained by the use of a sodium flame (burn an alcohol lamp containing a little salt dissolved in the alcohol), — all of the colors will appear yellow, or dull yellow or black.

The color shown by a body is due to the combination of all the rays of light which it reflects. When the character of the light which illuminates the body is changed, it will no longer reflect certain rays of light, and the color of the body will change. Certain dyes and combinations of dyes are exceedingly sensitive in this respect. If the quality of the light which illuminates such a color changes in the slightest degree, — a tinge bluer or redder, — the whole aspect of the color changes. All such shades appear very red in gas or lamp lights, because these lights are deficient in blue rays; and flatter or bluer in a bluish light, such as comes from a clear sky, on account of the deficiency of red in such a light.

It is possible, by combining specially selected dyestuffs, to produce two or three shades which will appear similar to each other in daylight, yet widely different by lamplight. Advantage has been taken of this property in producing fabrics which appear quite different in the day and at night.

The dyer sometimes has great difficulty in matching compound shades which are so sensitive that their aspect varies with the slightest change in the quality of even the daylight. The color may be matched all right in the forenoon, and be sadly off in the afternoon.

Such difficulties may be removed in two ways: —

(1) By avoiding dyestuffs with very sensitive colors. This is not always possible.

(2) By providing a light which does not change. The electric arc-light, shaded by colored glass so that its light will be the same as that of normal daylight, seems to give the best results in this respect.

Color-blindness. — Color-blindness is the inability to distinguish between certain colors, particularly between red and green. Pink appears blue; there is not much difference between the color of a stick of red sealing-wax and grass by day. A florid complexion appears dusky blue. Sometimes the color-blind persons pick out the red color correctly, but after a while their eyes seem to become fatigued, and they commence to select wools of a different color, generally green, and place them on the red heap.

Before beginning the study of dyeing, every student should be tested for color-blindness. He should be given a number of skeins of wool, and required to assort them according to their color, and he should also be required to name the colors of a number of samples. Ignorance of the names of colors should not, however, be mistaken for color-blindness. About one person in thirty or forty is color-blind.

Dye Testing. — In order to ascertain the properties of a dye, its suitability for mixing, its fastness, etc., the dyer conducts experimental dye-trials by methods similar to those adopted for experiments in this book, using as nearly as possible the methods and reagents actually used in the dye-house. By such experiments, he is able to obtain results which may be applied to his practical work. For example, he may ascertain what dyes are necessary, and in what proportions, to produce a desired shade of a given degree of fastness.

The methods for testing the fastness of a dye have already been given.

Comparative Dye-trials. — The object of comparative dye-trials is usually to ascertain which of the two or more samples of dyes is the least expensive. They may also be made to compare a sample of a dye with the consignment. Usually the samples are different samples of the same dye.

Comparative dye-trials must be conducted under exactly the same conditions, if the two samples are samples of the same dye, as a slight variation in temperature or volume of water in one of the dye-baths causes a considerable difference in the results. The amount of the dye used must not be large — not nearly sufficient to produce full shades; it is difficult to discriminate between deep shades of color, and again, if too much dye is used, much of it may be left in the bath, and probably in unequal quantities. As a rule, the methods to be followed should be similar to those used on a large scale. Fine woolen yarn is best for dye testing, even of dyes to be used on cotton, as it exhausts the bath more readily than cotton.

There are two cases to be considered: (1) a comparison of money values, and (2) a comparison of coloring power. The first one is usually made by the dyer, the second one, by the dye dealer in testing his wares so as to bring them (by dilution) to a standard strength.

(1) In comparing money values, simply dye equal weights of wool or cotton with quantities of dye in inverse proportion to their prices. For example, if two samples of fuchsine are to be compared, which cost 25 and 35 cents a pound respectively, we could make up a solution of 1 g. of each in a liter of water, and dye a 10-gram skein of wool with 50 cc. of the first, and $\frac{50 \times 25}{35} = 35.5$ cc. of the second. The skein which comes out darker would show which was *cheaper*. The purity of the color should also be considered.

(2) The relative coloring power is more difficult to ascertain. We would first dye two skeins with equal quantities of the dyes — say 50 cc. of the solution named above. After drying, the test is repeated, using 50 cc. of the *weaker* dye, and making three or more tests with the stronger one, using 25, 30, and 35 cc., or whatever volume that one judges would produce the same shade as the other. This is repeated until the two match.

Experiment 78. — You will be given two samples of a basic dye. The tests must be carried out under as nearly the same conditions as possible. Weigh out very carefully $\frac{1}{2}$ g. of each dye, and dissolve separately in 1000 cc. water, in a graduated flask, heating if necessary. See that the solution is complete.

Add 50 cc. of each solution, measured with a pipette, to two beakers, and make the volume of the solutions 200 cc. Place both beakers in the same water bath, heat to 60° C., enter a skein of wool into each beaker, and heat for an hour. Remove, wash, dry, and compare the colors.

If the colors are different, repeat, making one dyeing with one dye, and two or more with the other dye at the same time, using 50 cc. of one dye and the quantity of the other dye that you think will give the same shade; and also, in other beakers, 5 cc. less and 5 cc. more than this quantity. Continue to test until you get two skeins to match exactly. Then the volumes of the two dyes required to produce the same shade have the same coloring power. For example, if 50 cc. of A and 20 cc. of B are used, the strengths of A : B are as 20 : 50.

Testing for Mixtures. — Many dyes on the market are mechanical mixtures of two or more colors. In some cases the mixture is made to produce a "new" dye. In other cases the mixture is made because the dyer wishes to produce a certain color, and the quantity of one ingredient is so small that it cannot be weighed accurately by the dyer himself. Mixtures may be recognized: —

(1) By moistening a filter paper with water and blowing a small quantity of dye on it. Each particle of dye dissolves with its own color, and it may be readily seen whether two or more colors are present. It is even possible to form an idea of the relative proportions of the different constituents in this way. If the dye is insoluble in water, alcohol may be used. Valuable information may also be gained by dusting a few particles of the dye on concentrated sulphuric acid in a shallow dish, and observing the color with which they dissolve, which is usually different from that of the original dye.

(2) By successive dyeings. If a small dye-bath is prepared and several skeins dyed successively therein, if the coloring matter is pure, it will give a shading down of the same color; but if it is not, the first and last dyeing may be quite different. In applying this test it must be remembered that many dyes come on the market in an imperfectly purified condition, and also that light and dark shades of the same dye may naturally differ somewhat in color (tone) as well as in depth of color.

Experiment 79. — Test six samples of dye as follows: —

Place a small quantity of the dye on a piece of paper, dip a filter paper in water, hold it up, and blow the dye on the paper. Each particle dissolves with its own characteristic color.

Another way is to dust a little dye on the paper, and then wet it by floating it in a beaker of water. For dyes not soluble in water, alcohol may be used.

Detection of Dyes. — The large number of artificial colors now on the market renders the identification of a particular dye a matter of great difficulty. The color to be tested may be in the powder form or dyed on a fabric. In the latter case, the matter is still further complicated by the fact that few dyeings are made with a single color but mainly with mixtures.

It is beyond the limit of this work to go into details in regard to this matter. The powder or fabric is subjected to the action of a number of reagents, and the behavior of the color noted. Parallel tests are then made with the dye suspected of being present. The reagents used are concentrated sulphuric acid (see Exp. 12); dilute sulphuric acid or hydrochloric acid; dilute nitric acid; a solution of tannic acid and sodium acetate; reducing agents, as zinc dust and acetic acid (Exp. 3); sodium hydroxide and ammonia (Exp. 15); alum, potassium bichromate, ferric chloride, stannous chloride, and bleaching powder.

Except for the test with concentrated sulphuric acid, for which the dry powder is used, 1 g. of the dye should be dissolved or suspended in a liter of water, and portions of about 20 cc. taken for the tests. In the case of fabrics, portions of the material are cut off and subjected to the action of the reagents in porcelain evaporating dishes.

INDEX

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